

Coherent optical and spin control of Eu^{3+} -based molecular complexes for quantum information applications

Evgenij Vasilenko



Karlsruhe 2025

Coherent optical and spin control of Eu^{3+} -based molecular complexes for quantum information applications

Zur Erlangung des akademischen Grades eines
DOKTORS DER NATURWISSENSCHAFTEN (Dr. rer. nat.)

von der KIT-Fakultät für Physik des
Karlsruher Instituts für Technologie (KIT)
angenommene

DISSERTATION

von

M.Sc. Evgenij Vasilenko

Tag der mündlichen Prüfung: 27.06.2025
Erster Gutachter: Prof. Dr. David Hunger
Zweiter Gutachter: Prof. Dr. Mario Ruben

*Эта работа посвящается моим бабушкам и дедушкам —
бабе и деду Ильг,
а также с любовью и светлой памятью
бабе и деду Василенко —
с глубокой благодарностью за ценности и любовь,
которые они передали моим родителям
и которые сопровождают меня по сей день.*

*Diese Arbeit widme ich meinen Großeltern –
Oma und Opa Ilg
sowie in liebevoller Erinnerung Oma und Opa Vasilenko –,
in großer Dankbarkeit für die Werte und die Liebe,
die sie an meine Eltern weitergegeben haben
und die auch mich bis heute begleiten.*

Zusammenfassung

Das zunehmende Forschungsfeld optisch adressierbarer und spintragender molekularer Systeme entwickelt sich gegenwärtig als vielversprechende Alternative zu traditionellen festkörperbasierten Quantenemittern. Diese molekularen Systeme bieten spezifische Vorteile: ihre chemische Struktur sowie das Ligandenumfeld können durch gezieltes chemisches Design präzise angepasst werden, um die Materialeigenschaften zu verbessern, indem die Dekohärenzmechanismen von optischen und spinbasierten Übergängen reduziert werden. Diese Arbeit präsentiert eine umfassende experimentelle Untersuchung von fünf Eu^{3+} -basierten molekularen Komplexen mit dem vorrangigen Ziel, vielversprechende Kandidaten für zukünftige Quanteninformationsanwendungen zu identifizieren.

Der Referenzkomplex $[\text{Eu}(\text{BA})_4(\text{pip})]$ diente dabei als Grundlage für die Entwicklung und Validierung aller spektroskopischen Methoden, die im Verlauf dieser Arbeit angewandt wurden. Durch die systematische Charakterisierung der Referenzprobe $[\text{Eu}(\text{BA})_4(\text{pip})]$ mittels der Ensemblespektroskopie, die Photolumineszenzanregungsspektren, spektrales Lochbrennen, freien Induktionszerfall sowie Photonechos umfasst, wurde ein experimenteller Rahmen geschaffen, der auf alle weiteren Proben angewendet werden konnte. Unter den untersuchten molekularen Komplexen erwies sich der dinukleare Komplex $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$ als besonders vielversprechend, da es nach $[\text{Eu}(\text{BA})_4(\text{pip})]$ erst das zweite System ist, an dem ein eindeutiges Photonechosignal beobachtet werden konnte. Die daraus bestimmte optische Kohärenzzeit beträgt $1.96 \mu\text{s}$. Zudem bietet die dinukleare Struktur von $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$ die Möglichkeit, ein Zwei-Qubit-Gatter zu realisieren, das über elektrische Dipol–Dipol-Wechselwirkungen kontrolliert werden kann. Eine weitere bemerkenswerte Beobachtung bei den meisten Eu^{3+} -basierten Komplexen ist die lange Hyperfeinlebensdauer, die im Fall von $[\text{Eu}(\text{trensall})]$ etwa 8 min beträgt und auf gute spinbasierte Kohärenzeigenschaften hindeutet. Die Referenzprobe $[\text{Eu}(\text{BA})_4(\text{pip})]$ wies darüber hinaus eine sehr schmale inhomogene Linie mit einer Breite von 1.95 GHz auf, die deutlich geringer ist als der in der Literatur berichtete Wert [1]. Diese Verbesserung wurde durch die erfolgreiche Rekristallisation makroskopischer Einkristalle erzielt, die im Vergleich zu Pulver oder mikrokristallinen Proben eine bessere strukturelle Ordnung besitzen. Auch die extrem schmalen spektralen Löcher motivierten weitere Untersuchungen solcher makroskopischer Materialien.

Angeichts des bestehenden Bedarfs an überzeugenden Spineigenschaften in molekularen Systemen, wobei insbesondere in Eu^{3+} -basierten Komplexen noch keine Spinsignatur nachgewiesen werden konnte, wurde der Fokus anschließend auf deren gezielte

Untersuchung gelegt. Durch die Integration einer zylindrischen Hochfrequenz-Spule in den kryogenen Aufbau konnten erstmals optisch detektierte Kernspinmagnetresonanzen auf beiden Hyperfeinübergängen des Isotops $^{151}\text{Eu}^{3+}$ gemessen werden. Dadurch gelang es, eine kohärente Kontrolle des Kernspins mittels Rabi-Oszillationen zu demonstrieren. Anschließend erfolgte eine erste Bestimmung der Spinkohärenzzeit von $613\text{ }\mu\text{s}$, die über ein Spinecho-Experiment gemessen wurde. Die Verwendung von dynamischer Entkopplung über die CPMG-Pulssequenz verlängerte die Spinkohärenzzeit auf 2 ms . Diese Ergebnisse stellen einen Meilenstein in der Spincharakterisierung von auf seltenen Erden basierenden molekularen Systemen dar.

Neben der Spektroskopie wurde auch ein neuartiger, tieftemperaturtauglicher optischer Fabry–Pérot-Resonator auf Basis einer scannbaren Piezoröhre entwickelt, der bei Raumtemperatur Scanbewegungen in alle drei Raumrichtungen ermöglicht. Das System erreichte eine passive Stabilität von 0.7 nm RMS bei Raumtemperatur und 12.25 pm RMS bei einer Temperatur von 100 mK . Obwohl die laterale 2D-Rasterscannfähigkeit bei tiefen Temperaturen durch die verringerte Piezoauslenkung eingeschränkt wurde, konnte die mechanische Robustheit des Aufbaus in den ersten Experimenten bestätigt werden.

Zusammenfassend kann festgehalten werden, dass diese Arbeit erstmals eine vollständige optische und spinbasierte Kohärenzcharakterisierung eines mit Selten-Erd-Ionen integrierten molekularen Emittersystems liefert, die als Grundlage für die Identifikation vielversprechender Materialien für Quanteninformationsanwendungen dienen kann. Mit weiteren Fortschritten in der Materialsynthese, der Integration in optische Resonatoren sowie der Erforschung und Reduktion von Dekohärenzmechanismen könnten molekulare Quantensysteme zunehmend an Bedeutung gewinnen und sich potenziell zu skalierbaren, robusten Plattformen für zukünftige Quantentechnologien entwickeln.

Abstract

The growing field of optically addressable, spin-bearing molecular systems is currently emerging as a promising alternative to traditional solid-state quantum emitter platforms. These molecular systems offer distinct advantages: their chemical structure and ligand field environment can be precisely tailored through chemical engineering to improve material properties by reducing dephasing mechanisms of optical and spin transitions. This thesis presents a comprehensive experimental study of five Eu^{3+} -based molecular complexes, with the main objective of identifying promising candidates for future quantum information applications.

The reference molecular complex $[\text{Eu}(\text{BA})_4(\text{pip})]$ served as the basis for developing and validating all spectroscopic techniques employed in this thesis. Through the systematic characterization of $[\text{Eu}(\text{BA})_4(\text{pip})]$ via ensemble spectroscopy, including photoluminescence excitation scans, spectral hole burning, free-induction decay, and photon echoes, we established a robust experimental framework that can be applied to all other samples. Among the studied complexes, the dinuclear $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$ complex emerged as a promising candidate, demonstrating an optical coherence time of $1.96\ \mu\text{s}$ and making it, together with $[\text{Eu}(\text{BA})_4(\text{pip})]$, the second sample in which a clear photon echo could be observed. Moreover, $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$ is a dinuclear complex that could potentially serve as a candidate for realizing a two-qubit gate controlled via electric dipole–dipole interactions. Remarkably, most of the investigated Eu^{3+} -based molecular complexes exhibited long hyperfine lifetimes reaching up to 8 min for $[\text{Eu}(\text{trensar})]$, indicating promising spin coherence properties. The reference sample $[\text{Eu}(\text{BA})_4(\text{pip})]$ itself showed a significantly narrower inhomogeneous linewidth of 1.95 GHz than previously reported in the literature [1], a result attributed to the successful growth of macroscopic single crystals, which offer improved structural order compared to microcrystalline or powder samples. Additionally, these macroscopic crystals revealed exceptionally narrow spectral holes, motivating further investigation of macroscopic geometries for future studies.

Given the demand for molecular materials with improved spin properties, and in particular, the absence of any previously observed spin features in Eu^{3+} -based molecular systems, we devoted increased effort to exploring this aspect in more detail. By integrating a cylindrical RF coil into our cryogenic setup, we were able to perform optically detected nuclear magnetic resonance measurements on both hyperfine transitions of the $^{151}\text{Eu}^{3+}$ isotope. This enabled us to demonstrate, for the first time in such a system, coherent nuclear spin control through Rabi oscillations. Subsequent spin echo measurements revealed an intrinsic spin coherence time of $613\ \mu\text{s}$, which was further extended to

2 ms by employing the CPMG dynamical decoupling sequence. These results represent a significant milestone in the spin characterization of rare-earth-ion-based molecular systems.

Alongside the ensemble spectroscopy, significant progress was made in the development of the experimental setup. In particular, this thesis introduces a new cryo-compatible fiber-based Fabry–Pérot microcavity based on a piezoelectric scanner tube, enabling full 3D scanning capabilities at room temperature. The system achieved 0.7 nm RMS passive stability at room temperature and 12.25 pm RMS at a temperature of 100 mK. While 2D raster scanning was limited under cryogenic conditions due to reduced piezo expansion, the setup proved its mechanical robustness in initial experiments.

In conclusion, this thesis presents the first complete optical and spin coherence characterization of a rare-earth-ion-based molecular emitter system, providing a foundation for identifying promising candidates for quantum information applications. With further progress in material synthesis, cavity integration, as well as the investigation and mitigation of decoherence mechanisms, molecular quantum emitters are expected to gain in importance and could evolve into scalable and robust platforms for future quantum technologies.

Contents

1. Introduction	1
1.1. State-of-the-art quantum emitters	3
1.2. Rare-earth ions for quantum information applications	5
1.3. Spin-bearing molecules as optically addressable platforms	8
1.4. Outline of this thesis	10
2. Roadmap for Eu³⁺-based quantum technologies	13
2.1. Rare-earth elements	14
2.1.1. Energy level structure	16
2.1.2. Selection rules for $4f \rightarrow 4f$ transitions	19
2.1.3. Crystal field theory: a brief overview	20
2.2. Line broadening mechanisms	25
2.2.1. Natural linewidth	25
2.2.2. Homogeneous line broadening	26
2.2.3. Inhomogeneous line broadening	33
2.3. Eu ³⁺ -based materials	35
2.4. Toward REI-based quantum information applications	36
2.4.1. DiVincenzo criteria for quantum information applications	37
2.4.2. Proposed concept of REI-based quantum architecture	43
3. Experimental setup	47
3.1. Laser system	48
3.1.1. Frequency-selective elements	50
3.1.2. Laser stabilization	51
3.2. Optical setup and experimental control	53
3.2.1. Excitation path	55
3.2.2. Detection path	56
3.2.3. Frequency and amplitude modulation	58
3.3. Cryogenic environment	62
3.3.1. Dipstick cryostat	63
3.3.2. Dilution refrigerator	70
3.4. Description of fiber-based ferrule sample holder	74
4. Ensemble spectroscopy of Eu³⁺-based molecular complexes	81
4.1. Excitation processes and phonon-assisted dephasing mechanisms in molecular materials	82

4.2.	Experimental methods	85
4.2.1.	Optical properties	85
4.2.2.	Spin properties	96
4.3.	Measurements on Eu^{3+} ensembles in molecular complexes	102
4.3.1.	Analysis of the molecular complex $[\text{Eu}(\text{BA})_4(\text{pip})]$	102
4.3.2.	Analysis of the molecular complex $[\text{Eu}(\text{trens al})]$	127
4.3.3.	Analysis of the molecular complex $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$	132
4.3.4.	Analysis of the molecular complex $[\text{Eu}(\text{btfa})_3(\text{bipy})]$	135
4.3.5.	Analysis of the molecular complex $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$	141
4.4.	Conclusion of the investigated molecular complexes	146
5.	Implementation of a new microcavity design for spectroscopy	149
5.1.	Brief theoretical summary on optical resonators	150
5.2.	Design of a novel robust fiber-based Fabry–Pérot microcavity	155
5.3.	Integration into optical system and cavity performance	157
5.3.1.	Preparation of the piezo scanner tube	157
5.3.2.	Optical system and control unit	158
5.3.3.	Room temperature and cryogenic characterization	160
5.3.4.	Conclusion of the cavity implementation	167
5.4.	Outlook: toward cavity spectroscopy	168
6.	Summary and outlook	173
Appendices		179
A.	Overview of the ensemble spectroscopy pulse parameters	181
B.	Details on the coil geometry and the calculation of the magnetic field	184
C.	Cross-sectional view of the Sionludi	186
D.	Abbreviations	187
E.	Publications and conference contributions	190
Bibliography		193
List of Figures		207
List of Tables		211

1. Introduction

Just as time does not stand still, technological progress also continues to advance relentlessly. The pursuit of knowledge and the discovery of new phenomena have always been among the greatest driving forces behind scientific and technological advancement of human society.

The year **2025** marks a special date, as the scientific community celebrates the *100th anniversary* of quantum mechanics, a theory that revolutionized our perspective as well as our understanding of reality and nature at its most fundamental level. For this reason, the United Nations declared the year **2025** to be the **International Year of Quantum Science and Technology** [2]. The origins of quantum mechanics trace back to the start of the 20th century, around 1900, where physicists such as **Max Planck** and **Albert Einstein** started to describe subatomic phenomena, which could not be accurately explained by classical mechanics. The extraordinary breakthrough came in 1925, when **Werner Heisenberg** submitted the first consistent formulation of quantum mechanics to the journal *Zeitschrift für Physik* in a paper titled "*On the quantum-theoretical reinterpretation of kinematic and mechanical relationships*". Although complementary studies by **Max Born** and **Pascual Jordan**, as well as an alternative but mathematically equivalent formulation by **Erwin Schrödinger**, followed shortly thereafter, the work of Heisenberg laid the foundation for a scientific revolution that continues to shape modern physics and technology.

The revolution did not arise from discarding the laws of classical mechanics, but from a more radical reinterpretation of classical concepts such as energy and momentum, and from the realization that natural phenomena exhibit an inherent unknowable character at the quantum level, while classical physics constitutes an approximate representation of reality at the macroscopic level [2].

"What we observe is not nature itself, but nature exposed to our method of questioning." — Werner Heisenberg

Since its foundation, quantum mechanics has led to remarkable technological developments, from transistors and lasers to modern communication systems, including those based on quantum cryptography. Today, as we are part of the so-called **Second Quantum Revolution**, efforts are increasingly focused on exploiting quantum phenomena in order to realize advanced quantum technological applications in the field of computing, communication, and sensing.

The idea of using quantum mechanics not just to explain natural phenomena, but as a resource for computational processes, was first seriously proposed in the early 1980s. **Richard Feynman** and **David Deutsch** were among the pioneers and visionaries who suggested that certain physical processes could be simulated much more efficiently with quantum systems than with classical computers, as they can solve certain problems more efficiently [3]. These classical limitations were emphasized by Richard Feynman during his famous conference talk in 1981, where he stated [4]:

"Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy." — Richard P. Feynman

Based on these early ideas, David Deutsch formalized the concept of a universal quantum computer in 1985, proposing a theoretical model that could simulate any physical process and perform any computation achievable by a classical machine, potentially with greater efficiency. Quantum computing aims to harness the principles of quantum mechanics in order to perform computations that are infeasible even for the most powerful classical computers. Unlike classical computers, which store and process information using binary bits (zeros and ones), quantum computers rely on quantum bits, or *qubits*, which can exist in superpositions of multiple quantum states simultaneously and thus scale exponentially. By understanding and exploiting the key principles of quantum mechanics such as *superposition*, *entanglement*, *decoherence* and *interference*, quantum computers are capable of exploring multidimensional computational spaces, allowing them to solve complex problems involving an enormous number of interacting variables. For instance, the behavior of novel material systems in chemistry and material science could be simulated and predicted, resulting in cost- and time-efficient research processes, as not every slight modification to the molecular structure would require to be synthesized and investigated experimentally [5].

The field of quantum computing continued to develop rapidly, culminating in significant algorithmic achievements. One of the most notable algorithms was introduced in 1994 by the mathematician **Peter Shor**, who proposed a first practical real-world application for a quantum computer. The so-called *Shor's algorithm* proved to be a powerful tool, enabling the efficient factorization of large integers, which is generally considered as a hard computational task for classical computers. For this reason, many advanced cryptographic protocols were based for a long time on integer factorization. Shor's algorithm demonstrated the theoretical power of quantum computers, highlighting their ability to solve certain classes of problems exponentially faster than classical machines, reducing processing times from thousands of years to just a few minutes. Based on these insights, which had far-reaching implications for potential applications, worldwide efforts were initiated to develop quantum computers and explore new quantum technologies. The resulting need for scalable, highly coherent and controllable quantum systems thus triggered an intensive search for promising material platforms and quantum emitters that fulfill the key requirements for reliable quantum operations, which are formally

summarized by the *DiVincenzo criteria* [3] and will be discussed in detail in the following chapter.

Beyond its implications for cybersecurity, Shor's algorithm could find applications in industries characterized by complex data structures and computational challenges. Potential future applications include accelerating the discovery of new pharmaceuticals, designing sustainable chemical processes, optimizing supply chains, and advancing machine learning techniques [5].

1.1. State-of-the-art quantum emitters

A wide range of quantum emitter systems has been investigated in recent years, each offering distinct advantages depending on the specific requirements of the targeted application in quantum information processing (QIP). The most prominent examples include trapped ions, color centers in diamond, semiconductor quantum dots, and rare-earth ions doped into solid-state materials. In the following, the mentioned emitter systems will be briefly introduced.

Trapped ions: The use of trapped ions has proven to be a promising way of implementing quantum technologies, offering long coherence times, high-fidelity gate operations, and especially precise individual qubit control. Single ions can be confined for long durations by using laser cooling and electromagnetic traps such as *Paul* or *Penning traps*, and can be coherently manipulated, as they experience only small perturbations from the environment or fluctuating noise. Quantum information is typically encoded in hyperfine or electronic states, while the motional degrees of freedom can be used for entangling operations between ions. When a group of ions is trapped, they form a linear *string* within the applied electromagnetic potentials, where each ion can be stored for long durations and localized in space within a range of a few nanometers. Tightly focused laser beams are required to enable coherent manipulation of individual ions. The demonstrated key properties include coherence times as long as 10 min for superpositions of two hyperfine states of a single ion, as well as high single-qubit and two-qubit gate fidelities exceeding values of 0.99. These attributes make trapped ions a robust emitter system for testing fundamental elements of quantum computation. Nevertheless, operational errors still need to be reduced, and the number of ions must be substantially scaled up to enable practical quantum computing. The associated challenges comprise the increasing complexity of trap architectures and control systems as the number of ions grows [6, 7, 8].

Defect color centers in diamond: Color centers in diamond, such as the nitrogen-vacancy (NV) center and, in particular, group-IV defects including silicon-vacancy (SiV), germanium-vacancy (GeV), tin-vacancy (SnV), and

lead-vacancy (PbV) centers, have emerged as promising candidates for quantum information applications. The NV center consists of a substitutional nitrogen atom adjacent to a vacant carbon lattice site in the diamond structure, providing optical addressability and long-lived spin states. However, it suffers from spectral diffusion, introduced by the fluctuating charge environment, and a low rate of indistinguishable coherent photon emission. In contrast, group-IV defects feature a split vacancy configuration, where the impurity atom is symmetrically positioned between two vacant carbon sites, resulting in stable optical transitions as well as accessible electronic and hyperfine spin states, protected by inversion symmetry [9, 10]. Compared to the widely studied NV center, group-IV defects exhibit significantly higher *Debye-Waller factors* (with maximum values reaching up to $\approx 70\%$, compared to only 3% to 4% for NV centers), indicating a much larger fraction of emission into the zero-phonon line (ZPL) and a reduced sensitivity to electric field fluctuations. Considering the *quantum efficiency*, which is defined as the ratio of radiative to total decay, then the SnV center shows favorable performance, with reported values around 80%. For quantum communication and entanglement-based applications, a high product of Debye-Waller factor and quantum efficiency is essential, as it represents the yield of coherent photons. In addition, group-IV color centers possess large ground-state splittings (e.g., 820 GHz for SnV), which can suppress phonon-induced spin decoherence and enable experimental operation at temperatures above 1 K, avoiding the need for continuous cooling to the millikelvin regime, which is required by defect centers with smaller splittings like in the case of the SiV center. As a result, demonstrated coherence times range from a few microseconds to a few milliseconds when applying dynamical decoupling control techniques. Notable key achievements and demonstrations using NV or group-IV color centers include the remote entanglement of two spatially separated qubits, loophole-free Bell tests over a kilometer-scale distance, and the realization of multi-node quantum networks based on NV and SiV centers. Nevertheless, while each color center offers distinct advantages, ongoing challenges still remain, particularly regarding the improvement of fabrication techniques, charge-state stabilization, and the mitigation or even suppression of temperature-dependent spin relaxation processes [11, 12, 13, 14].

Semiconductor quantum dots: Semiconductor quantum dots (QDs) are nanostructured clusters of semiconductor material that confine charge carriers such as electrons, holes, or excitons, in all three spatial dimensions, resulting in discrete and atom-like energy levels. This quantum confinement can be initially illustrated by electrons trapped in quantum wells, where confinement occurs in only one spatial direction. In QDs, confinement is extended to all three dimensions, typically achieved by embedding a thin layer of a low band gap material (such as InAs or InGaAs) within a higher band gap material (such as GaAs), forming a heterostructure. By carefully choosing the structure of the material system and controlling the size of the QDs, the *density of states*, which represents the number of available energy levels in a particular small energy range, as well as the degree of confinement, can be precisely tuned. A fascinating property of QDs is that they can self-assemble during epitaxial growth processes, including molecular

beam epitaxy or metal-organic chemical vapor deposition, enabling scalable fabrication of novel photonic devices. Due to the strong confinement, QDs feature quantized optical and electronic transitions, making them so-called *artificial atoms*. Typical energy level separations range from tens to hundreds of meV, well above the thermal energies at cryogenic temperatures, thus maintaining discrete energy spectra. The atom-like optical properties of the QDs, characterized by strong optical dipole moments, result in bright, on-demand single-photon sources, which constitute an important building block for quantum communication and photonic quantum computing. Under optimized conditions, QDs can achieve optical transitions with sharp linewidths limited only by their natural radiative lifetime, enabling highly coherent and indistinguishable single-photon emission. However, as QDs generally emit photons isotropically and not in a directed manner, the collection efficiencies of indistinguishable photons are typically low without additional photonic engineering. By embedding QDs in nanophotonic structures such as micropillars, photonic crystals, Fabry-Pérot microcavities, and waveguides, near-unity photon indistinguishability ($> 95\%$) and high single-photon extraction efficiencies exceeding 80% have been demonstrated. Furthermore, the spin states of confined electrons or holes can be used as stationary spin qubits, with reported spin coherence times ranging from several nanoseconds to a few microseconds depending on the material composition and the degree of hyperfine interactions with the surrounding nuclear spins (fluctuating local magnetic field). Compared to other emitter systems, these coherence times are relatively short. Additional challenges include fabrication issues, as the bare materials tend to deteriorate and require protective layers, spectral diffusion leading to inhomogeneously broadened transitions, as well as the optimization of the deterministic integration processes into photonic devices [15, 16, 17].

While the previously described quantum emitter systems have demonstrated remarkable progress toward scalable quantum technologies, *Rare-earth ions (REIs)* are particularly promising as optically addressable qubits due to their exceptional coherence properties. Given their central role in this work, REIs will be introduced in the following section and discussed in greater detail in Chapter 2.

1.2. Rare-earth ions for quantum information applications

REIs doped into crystalline solid-state materials have emerged as outstanding candidates for QIP applications. Their exceptional spectroscopic properties originate from the shielding of the $4f$ electrons by outer filled $5s$ and $5p$ orbitals, protecting the optical transitions from environmental perturbations. As a consequence, this shielding leads to narrow homogeneous linewidths and thus long optical and spin coherence times, which are required for reliable quantum memories and quantum network nodes. A notable achievement is the observation of optical transitions as narrow as 100 Hz in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ and 50 Hz in $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ [18, 19]. When Rare-earth ion (REI) species possess non-zero nuclear spin, qubit encoding can be realized using the hyperfine ground states, fulfilling

all necessary requirements for optically addressable REI-based spin qubits. Reported nuclear coherence times range from tens of milliseconds up to several hours [20, 21]. In the next part, we discuss the current applications of REIs in quantum technologies and projects, focusing on demonstrated results and their relevance for future scalable REI-based quantum architectures.

Initial experimental efforts in REI-based quantum memories originated in the context of classical optical storage and signal processing systems in the 1980s and 1990s. However, the realization of such storage schemes required the use of photon-echo-based pulse sequences, which introduced additional noise in the local environment and thus dephasing due to strong optical rephasing pulses. This led to the development of alternative memory protocols, such as *Controlled Reversible Inhomogeneous Broadening (CRIB)* [22, 23], where strong optical rephasing pulses were omitted, achieving successful quantum information storage with efficiencies up to $\approx 69\%$ in $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$ [24]. Another reliable and more modern storage protocol, the so-called *Atomic Frequency Comb (AFC)*, was proposed by Afzelius *et al.* [25, 26, 27]. It takes advantage of strong absorption in an inhomogeneously broadened ensemble of atoms, particularly in REI ensembles. The protocol creates a periodic structure of narrow absorption lines with equal spectral spacing of Δ , created within the inhomogeneous linewidth of the corresponding ensemble to store and re-emit optical photons in a controlled and coherent way after a fixed delay time of $1/\Delta$. This process is very similar to common photon echo experiments [28].

As most protocols rely on exploiting hyperfine states to create a coherence, the major limitations in REI-doped crystals stem from local magnetic field fluctuations caused by spin flip-flops of nuclei of the host lattice. In order to overcome this, the *Zero First-Order Zeeman (ZEFOZ)* technique offers an effective solution for identifying external magnetic field configurations where the gradient of the hyperfine transitions becomes relatively small, so that the system becomes insensitive to magnetic fluctuations in any direction. The corresponding magnetic field points are called *ZEFOZ points*, which constitute avoided crossings of the hyperfine levels and exhibit a vanishing Zeeman interaction to the first order. Europium and praseodymium ions represent two ideal candidates to be used in ZEFOZ applications, as they naturally feature a high resilience to magnetic field variations due to an even number of $4f$ electrons and therefore zero unpaired electrons. First milestone results were achieved with the ZEFOZ technique in $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$ and $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$, with spin coherence times exceeding 1 min and up to 13 h, respectively, at cryogenic temperatures. In the case of REI species with an uneven number of $4f$ electrons, such as ytterbium and erbium, reported coherence times are in the range of ~ 1.5 ms, even without applying external magnetic fields [29, 30]. The advantages of these ions include a higher branching ratio into the coherent optical transitions and emission wavelengths directly in the near- as well as mid-infrared region, which is crucial for quantum communication applications and if given without the need for wavelength conversion (e.g., Er^{3+}). In view of the experimental effort required to determine potential ZEFOZ points, advancing theoretical modeling is essential. The combined use of crystal-field and spin-Hamiltonian modeling approaches has enabled

the prediction of ZEFOZ points across different REI species, thereby allowing one to further optimize the operating conditions of established material systems [28].

Recent advances have further pushed the limits of REI-based quantum memories. As previously stated, coherence times up to several hours have been observed in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ by operating the experiment at both a ZEFOZ point and at a cryogenic temperature of 1.4 K. In addition, dynamical decoupling sequences have been applied to extend the coherence time further, which leads to a decoupling of Eu^{3+} ions from the local host environment. By continuous cooling of the system to about 125 mK, spin impurities, constituting the major limiting factor at such temperatures, could be effectively suppressed and *frozen out*, extending the coherence time beyond 13 h. In the absence of spin impurities, the next most dominant dephasing mechanism results from the field inhomogeneity of the ZEFOZ point due to the spin inhomogeneous broadening. As a consequence, by spectrally selecting a narrow subensemble within the spin inhomogeneous broadening, even longer coherence times of more than 18 h have been observed, which is the longest reported coherence time for any optically addressable quantum emitter system used for a quantum memory to date [21]. It is also important to note that a temperature-dependent measurement series demonstrated the feasibility of achieving coherence times of up to 6 h at even higher temperatures around 6 K, enabling the use of less complex cryostats than dilution refrigerators [21]. These new milestones highlight the suitability of REI-based quantum emitter systems for a broad range of future quantum information applications.

As a final point, we emphasize a European research initiative that, over the past few years, has provided key conceptual and technological groundwork for realizing REI-based scalable quantum architectures. The *Scalable Rare-Earth Quantum Computing Nodes (SQUARE)* project outlined a comprehensive vision for building quantum processor nodes based on REIs. Considering the key requirements of scalable quantum nodes, there is no REI species that naturally fulfills all desirable properties simultaneously. However, new methods such as co-doping multiple REIs into a common solid-state host material could be employed to assign specialized tasks to different ion species within the same node and thus introduce coupled systems for storage as well as communication [31]. To realize quantum processor nodes based on REIs, several concepts have been proposed within the REI community, including ensemble-based schemes [32]. The SQUARE project focused on the single-ion strategy, targeting the individual addressing of hundreds to thousands of REI qubits per node with a promising interconnectivity between the qubits. A variety of different REI species were investigated to evaluate their suitability for scalable architectures. Recent simulation studies have confirmed the scalability and interconnectivity potential of this approach [33, 34]. Further details are discussed in Chapter 2.

Beyond traditional solid-state hosts, a growing field of research focuses on developing novel quantum materials based on molecular platforms, where electronic and recently nuclear spins can be optically addressed. In the following, spin-bearing molecules are introduced as an alternative class of emitters for quantum technologies.

1.3. Spin-bearing molecules as optically addressable platforms

An important addition to the previously introduced quantum emitter systems is provided by the emerging field of molecular platforms, which offer optically addressable spin states and the potential for highly tunable chemical structures through molecular engineering, with the aim of improving intrinsic material properties and opening up new perspectives for quantum information applications. In the following, we briefly discuss three major classes that are currently under active investigation.

Organic chromophores: Organic chromophore-based systems featuring electron spin states can be broadly categorized into two classes: **(i)** The first category involves chromophore-based systems coupled to stable radicals ($C-R\cdot$), where C and R denote the chromophore and radical, respectively, and polycyclic aromatic systems capable of undergoing singlet fission. The latter effect describes a process in which one optically excited singlet pair splits into two entangled triplet excitons of high spin-multiplicity (strong exchange interaction), offering the possibility of microwave manipulation and creating coherence between two electronic spin states. **(ii)** The second category considers radical-ion pair states formed through photo-induced electron transfer in electron donor(D)-bridge(B)-acceptor(A) structures (D-B-A system), which can be additionally tailored with radicals. Furthermore, molecular systems that can undergo symmetry breaking charge transfer (SBCT) can also be employed as spin qubits. SBCT refers to a process in which two identical chromophores, connected through a bridge, experience spontaneous charge separation upon photoexcitation due to induced fluctuations in the local environment that break the molecular symmetry. The resulting charge-separated states can be utilized for creating spin qubits. Both classes offer the advantage of chemical tunability and potentially strong absorption. However, the achieved electron spin coherence ($T_{2,e} \sim 10 \mu s$) is still relatively small and remains a central challenge [35].

Transition-metal complexes: The transition metals (TM), positioned in the fourth period of the periodic table, feature an incomplete 3d shell, whose corresponding energy level structure is very sensitive to their ligand environment. By carefully engineering the ligand field strength and symmetry, TM complexes with spectrally narrow metal-centered optical transitions and ground-state spin triplet states ($S = 1$) can be realized. According to Fataftah and Freedman *et al.* [36], TM complexes can be employed as optically addressable electron spin qubits if certain criteria are fulfilled. These include a zero-field splitting within the electron paramagnetic resonance (EPR) addressable range and a first electronically excited state acting as a spin singlet ($S = 0$). The resulting electronic structure allows for both off-resonant excitation involving intersystem crossing (ISC) processes and on-resonant, frequency-selective excitation, enabling the implementation of coherent control schemes. Recent advances demonstrated optical and

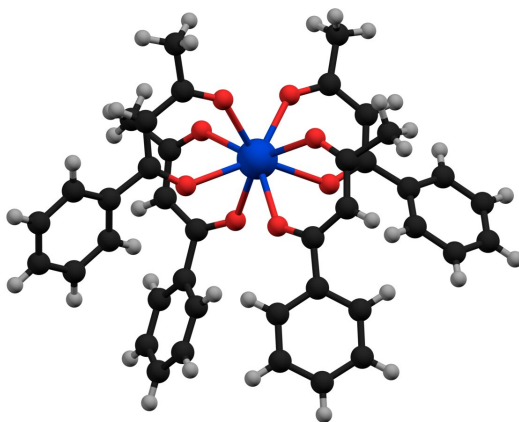


Figure 1.1: Exemplary europium-based molecular complex used throughout this thesis. The europium ion (blue) is located at the center and is surrounded by organic ligands composed of oxygen (red), carbon (black), and hydrogen (gray). Counterions are omitted for clarity.

spin coherence in TM complexes based on Cr^{3+} , Cr^{4+} , V^{3+} , V^{4+} , and Ni^{2+} ions. The TM complexes offer a versatile design space for the development of future quantum emitter systems. Nevertheless, the fundamental criterion of achieving long spin coherence times ($T_{2,e} \sim 10 \mu\text{s}$) must still be further improved [35].

REI-based molecular complexes: REI-based molecular complexes combine the shielding of the $4f$ electron manifold by the outer $5s$ and $5p$ orbitals with the design flexibility offered by molecular chemistry. As a result, their sharp optical lines are not strongly affected by the coordinating ligand field environment. Similar to REI-doped crystals, where exceptional optical and spin coherence properties have been demonstrated at cryogenic temperatures, Eu^{3+} -based molecular compounds have so far shown encouraging results. Ultra-narrow optical lines, long optical coherence times ($T_{2,o} \approx 60 \mu\text{s}$ for diluted samples), and long nuclear spin lifetimes of up to 5 min have been observed [1, 37]. Applications of REI-doped crystalline materials already span various areas of quantum technologies, including quantum memories, quantum communication, and quantum computing schemes. Embedding REIs into well-defined molecular environments could further allow fine-tuning of qubit figures of merit [35]. Although no spin coherence has yet been observed or reported in REI-based molecular compounds, Eu^{3+} ions offer an intrinsic nuclear spin for both the naturally occurring isotopes ($I = 5/2$). The successful implementation of reproducible coherent nuclear spin control — as demonstrated in this thesis — represents an important step toward advancing molecular REI systems for future quantum information applications. The molecular structure shown in Figure 1.1, which was initially studied by our collaborators [1] to provide initial spectroscopic characterization, served as the platform for achieving coherent nuclear spin control in

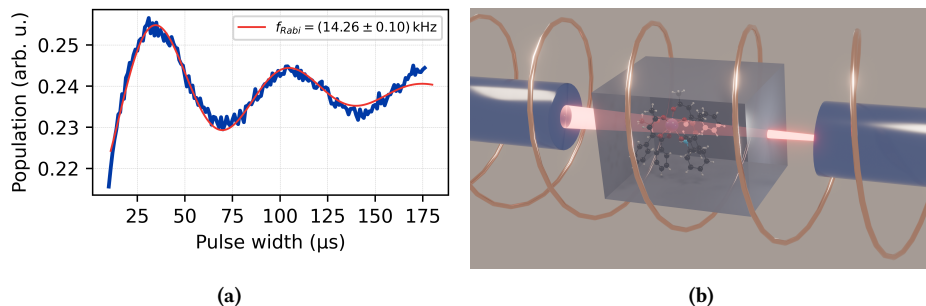


Figure 1.2: Demonstration of coherent nuclear spin control using RF driving. (a) Rabi oscillation of a hyperfine transition of a Eu^{3+} -doped molecular complex. (b) Rendered schematic of the fiber-based ferrule sample holder combined with an RF coil. The macroscopic crystal is represented as a rectangular volume, with the molecular structure shown inside to illustrate that the crystal is composed of molecular complexes.

this work, as demonstrated in Figure 1.2(a), with the corresponding experimental setup shown in Figure 1.2(b).

As this research field is still in its early stages, optically addressable spin-carrying molecules could potentially become a promising building block for quantum technologies, given that prerequisites such as scalable fabrication, tunable material properties, and the realization of spin-photon interfaces are feasible but require further analysis and improvement. After providing an overview of the current landscape of established quantum emitters and novel spin-bearing molecular systems, the following section outlines the structure of this thesis and briefly summarizes the content of each chapter.

1.4. Outline of this thesis

Molecular materials doped with REIs are increasingly moving into the focus of research for their potential to be implemented as optically addressable spin qubits [1, 37, 38, 39, 40]. A close collaboration between physical and chemical research groups plays a central role in this development, enabling the exchange of expertise between both fields. The core idea behind using molecular backbones is that chemical engineering of the ligand field environment allows tuning of material properties to improve their suitability for quantum information applications.

While the REI-based molecular complexes exhibit intrinsic coherent optical and spin properties, the main challenge, which is similar to other quantum emitter platforms, lies in minimizing the dephasing mechanisms. Achieving precise control in both optical and spin domains demands advanced experimental techniques and deeper theoretical

understanding, particularly since molecular REI systems have only recently started to be explored.

The principal aim of this thesis is to analyze and identify promising *europium-doped molecular candidates* for the integration into scalable REI-based quantum architectures. Several spectroscopic measurements were performed and optimized with a focus on coherence properties, guided by prior work on Eu^{3+} -doped solid-state hosts and molecular systems. Although coherent spin control in molecular materials is still at an early stage, with first experiments reported, for instance, on metal-organic molecular complexes by the research group of **Professor David Awschalom** [38], the results obtained so far demonstrate that spin qubits in molecular platforms are feasible. However, the measured coherence times still require substantial improvement compared to more established quantum emitter systems.

Within the scope of this work, we address critical aspects related to the optimization of ensemble spectroscopy for REIs and propose procedures for introducing coherent control of the nuclear spin of Eu^{3+} ions embedded in organic molecular structures. The results presented here encourage the continuation of efforts in the search for new molecular-based REI quantum systems. As a first experimental milestone, Figure 1.2(a) shows the initial demonstration of coherent control, achieved by driving hyperfine transitions of one of the investigated Eu^{3+} -doped molecular systems using a radio frequency (RF) coil. Nevertheless, further experimental and theoretical work is needed to fully verify the spin properties and to generalize the approach to other REI-based molecular complexes. In the following, we will provide an overview of central theoretical and experimental considerations covered or partially approached within this work:

- In **Chapter 2** we discuss the fundamental properties of REIs with the primary focus on Eu^{3+} -based material systems. This includes the derivation of the corresponding energy level scheme via the effective Hamiltonian comprising the Coulomb interaction, spin-orbit coupling, crystal-field effects, the hyperfine interaction, and Zeeman effects. Afterwards, several mechanisms of homogeneous and inhomogeneous line broadening are discussed, and two exemplary host materials are presented to provide first insights into Eu^{3+} -based systems. Furthermore, the DiVincenzo criteria for quantum computing are introduced and applied to REI systems. The chapter concludes with the presentation of a conceptual REI-based quantum architecture proposed by the SQUARE project.
- **Chapter 3** presents the realization of the experimental setup, including the laser system, optical excitation as well as detection paths, the experimental control unit, and the implementation of an RF infrastructure. The cryogenic environment used for low-temperature ensemble spectroscopy includes dipstick cryostats and dilution refrigerators. Finally, the design and modifications of the fiber-based ferrule sample holders are introduced, where different integration

methods had to be developed to meet the specific requirements of various cryostat platforms.

- **Chapter 4** forms the core of this thesis and introduces the theoretical background necessary to understand the structure and main processes of Eu^{3+} -doped molecular systems. The different procedures for sample preparation are then presented. Subsequently, the spectroscopic methods used to characterize the optical and spin properties are described in detail. Experimental results obtained for five different Eu^{3+} -doped molecular compounds are discussed, with particular focus on the identification of coherent optical and spin properties. In one candidate system, coherent spin control via RF driving of a hyperfine transition was successfully demonstrated, representing a first milestone toward employing REI-based molecular compounds as optically addressable spin qubits.
- **Chapter 5** begins with a discussion of the theoretical background of optical Fabry–Pérot cavities and the relevant parameters, when quantum emitters are coupled to them. Afterwards, a newly developed open-access microcavity for cryogenic experiments, based on a piezo tube design for modulating the cavity fiber mirror, is introduced. The performance of the cavity is characterized at room temperature and under cryogenic conditions, demonstrating its suitability for future quantum optical experiments. Finally, an outlook is provided based on first experimental insights into integrating molecular samples into the cavity for cavity-enhanced spectroscopy and the realization of coherent spin-photon interfaces.
- **Chapter 6** concludes the thesis by summarizing the main results and contributions presented throughout this work. Key achievements in the spectroscopic investigation of Eu^{3+} -doped molecular complexes and the development of a new cryogenic-compatible optical microcavity are highlighted. A final outlook is provided, discussing the main challenges and future perspectives of the project, with particular emphasis on improving the coherence properties of molecular REI systems and advancing the next steps toward their potential integration into scalable REI-based quantum architectures.

This structure is intended to build a coherent understanding, starting from the fundamental properties of REIs to the experimental realization of coherent control in molecular REI systems, culminating in a discussion of future experimental directions and suggestions for improvement in this emerging field.

2. Roadmap for Eu^{3+} -based quantum technologies

The realization of scalable quantum technologies has inspired many researchers to discover and investigate novel material platforms. Although the notion of a perfect system does not exist, several promising emitter systems have now been established that largely fulfill the key requirements and are already transitioning from unique demonstrations to scalable and commercially viable technologies. Among the many studied systems, a few notable examples include superconducting qubits, trapped ions, semiconductor quantum dots, and color centers in diamond (such as NV and SnV centers).

In this work, our focus lies on the study of REIs, in particular the investigation of new molecular host materials doped with Eu^{3+} ions. REI-based systems have long been studied due to their excellent coherence properties and robustness against environmental fluctuations. These characteristics arise from their underlying atomic structure, which naturally protects the electronic and nuclear states, making REIs particularly promising candidates for applications in quantum computing, quantum memories, and quantum communication.

This chapter provides the main ideas of the theoretical roadmap for implementing REIs into quantum architectures proposed by Adam Kinos *et al.* [33] in the scope of the *SQUARE* project, a European Flagship initiative. To understand the potential of these systems, it is essential to first review the fundamental properties of REIs, including their energy level structure and the corresponding mathematical description, their interaction with the surrounding crystal field of the host material, and the impact of other contributing mechanisms. Given that the primary focus of this work is on Eu^{3+} ions, all explanations will be illustrated using Eu^{3+} -based examples. To present additional context, two widely studied Eu^{3+} -based material systems, which have been successfully employed in many experiments, will be briefly introduced.

In order to determine the suitability of REI-based systems for quantum information processing, we first outline the DiVincenzo criteria, which summarize the essential physical requirements for realizing reliable quantum technologies. Subsequently, we compare these theoretical criteria with experimental results obtained in REI systems, highlighting their strengths and current limitations. Building upon these insights, we close this chapter with a presentation of the conceptual framework proposed within

Periods	Groups																18	
1	¹ H	2											13	14	15	16	17	² He
2																		
3			3	4	5	6	7	8	9	10	11	12						
4																		
5																		
6																		
7																		
	²¹ Sc																	
	³⁹ Y																	
	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			

Figure 2.1: Representation of the rare-earth elements. The periodic table highlights the rare-earth elements, including the lanthanide series as well as scandium and yttrium. Europium is marked in red to emphasize its central role in the experimental work presented in this thesis.

the SQUARE project, which envisions a scalable architecture for REI-based quantum technologies. Although the SQUARE project has concluded, the ideas developed during the project remain highly relevant and offer valuable guidance for future realizations of REI-based, and specifically Eu^{3+} -doped, quantum systems.

2.1. Rare-earth elements

The rare-earth elements are primarily found in the *lanthanide series*, which is located in the 6th period of the periodic table, including 15 elements with atomic numbers Z ranging from 57 (lanthanum, La) to 71 (lutetium, Lu). In addition, the elements scandium (Sc, $Z = 21$) and yttrium (Y, $Z = 39$) are commonly grouped with the lanthanides due to their similar chemical properties, especially when doped into solid-state host materials. Figure 2.1 highlights the position of all REIs within the periodic table. The predominant oxidation state in the rare-earth chemistry is the trivalent or triply ionized state (i.e., Eu^{3+}), nevertheless, other oxidation states also exist (i.e., Eu^{2+} or Tb^{4+}). The electronic configuration of trivalent lanthanides is based on the noble gas xenon with $[\text{Xe}]4f^N$ ¹, which has completely filled 5s and 5p orbitals, but empty 4f shells. Increasing the number N from 0 to 14 corresponds to a progressive filling of the 4f orbitals. Therefore,

¹ $[\text{Xe}] = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

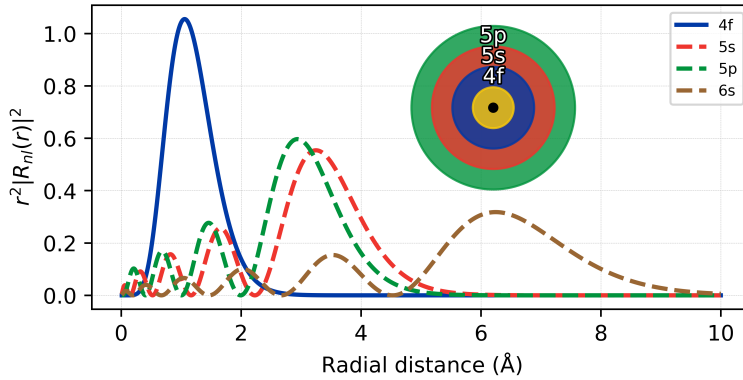


Figure 2.2: Radial probability density of the 4f, 5s, 5p, and 6s orbitals of Eu^{3+} . The main plot shows the radial probability density $P(r) = r^2|R_{nl}(r)|^2$ as a function of distance from the nucleus, illustrating the spatial extent and localization of the electron orbitals. Here, $R_{nl}(r)$ denotes the normalized radial wavefunction. The inset schematically represents the electron shells, highlighting the shielding of the 4f electrons by the outer 5s and 5p shells [42, 43].

the main chemical difference between the elements is the ionic size, which decreases steadily toward lutetium. This effect is also known as the *lanthanide contraction*, where the nuclear charge Ze increases with the atomic number Z across the lanthanide series, meaning that the additional electrons added in the 4f orbitals are poorly shielded from the nucleus. As a result, the effective nuclear charge experienced by the outer electrons increases and leads to a gradual decrease in ionic radii across the series [41].

The filled 5s and 5p orbitals are spatially located further outward than the 4f shell, as can be seen from the radial distribution of the electron orbitals in Figure 2.2. For this reason, the outer electrons interact more with the environment, which is why the chemical properties of the lanthanides are very similar, and their spectroscopic characteristics mainly differ due to the number of 4f electrons. The special feature here is that the 5s and 5p orbitals additionally act as a Faraday cage, thereby shielding the inner 4f shell from external influences or perturbations caused by the lattice [44]. The spectroscopy of triply ionized REIs is dominated by 4f $\rightarrow$ 4f transitions, resulting in narrow spectral lines due to this effective screening. Only with the development of tunable and narrowband laser sources did the spectral resolution no longer limit the measurements, and the inhomogeneously broadened features of these transitions could be studied. In order to probe the homogeneously broadened linewidth of these transitions, new spectroscopy techniques, such as spectral hole burning or various echo sequences, were established or adapted from nuclear magnetic resonance (NMR) spectroscopy, especially since these lines are narrower by a factor of up to 10^7 compared to the inhomogeneous linewidths [44].

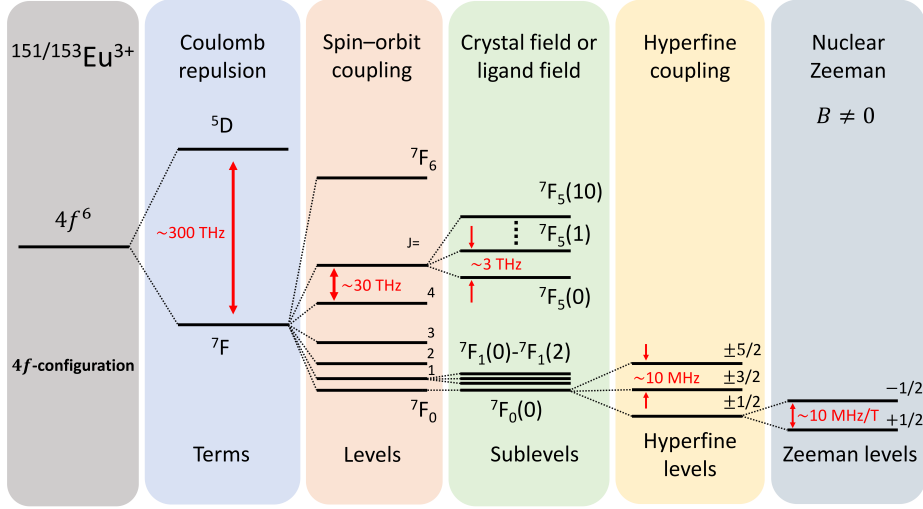


Figure 2.3: Energy level structure of an REI illustrated using the example of Eu^{3+} . The diagram schematically represents the hierarchy of energy splittings arising from various interactions within an REI: starting from the Coulomb interaction, followed by the spin-orbit coupling, crystal field splitting due to the host material lattice, the hyperfine and nuclear quadrupole interactions, and finally the nuclear Zeeman effect when an external magnetic field is applied. Each level of interaction further refines the energy level structure, determining the possible optical and spin transitions that can be harnessed for specific quantum measurement protocols. The values highlighted in red indicate the approximate order of magnitude of the corresponding energy splittings. Figure adapted from [45].

2.1.1. Energy level structure

The energy level structure of REIs arises from a complex interplay of several interactions, including Coulombic repulsion, spin-orbit coupling, crystal field or ligand field effects, and hyperfine interactions. A sketch of the relevant energy levels according to the respective interactions is illustrated in Figure 2.3, using trivalent europium (Eu^{3+}) as an example, since it serves as the primary ion species studied throughout this thesis.

Coulomb interaction: The dominant contribution to the large energy splittings is governed by the Coulombic repulsion between $4f$ electrons together with spin-orbit coupling. The Coulomb interaction splits the $4f^N$ configuration into multiple terms with separations on the order of 100 THz (10^4 cm^{-1}). A special case is represented by the rare-earth elements Ce^{3+} and Yb^{3+} , which have a single $4f$ electron and $4f$ hole, respectively. In these ions, term splitting due to Coulombic repulsion is absent, but spin-orbit coupling still causes splitting. The resulting terms from the Coulomb interaction are conventionally labeled using the *Russell–Saunders (LS)* term symbols.

Spin-orbit interaction: Spin-orbit coupling further splits these terms into multiplets, labeled using the Russell–Saunders notation $^{2S+1}L_J$ [46]. Here, S denotes the total spin angular momentum, L the total orbital angular momentum, and the total angular momentum J results from their vector sum $L + S$, taking values from $|L - S|$ to $L + S$ in integer steps. According to *Hund’s rules*, the ground state favors the lowest or highest possible J value, depending on the electron configuration, for instance, $J = |L - S|$ is favored when the subshell is less than half-filled. The orbital angular momentum quantum number L follows the historic spectroscopic letter notation $L = S, P, D, F, \dots$ corresponding to $L = 0, 1, 2, 3, \dots$. The separation of these $(2J + 1)$ terms is on the order of 10 THz (10^3 cm^{-1}) and constitutes the primary energy scale from which the transition frequencies of REIs can be determined [28, 47].

Crystal field interaction: When embedding REIs into a host material, such as solid-state crystals or molecular frameworks, they experience an electrostatic field induced by the surrounding ions in the crystal lattice. This interaction is known as the *crystal field effect*, while in molecular systems it is referred to as the *ligand field effect*, and can be treated as a host-dependent perturbation. Consequently, each multiplet further splits into so-called Stark levels on the order of 1 THz (10^2 cm^{-1}). The resulting number n of Stark levels depends on the site symmetry of the crystal field (CF) environment. In the following, the CF levels are labeled as $^{2S+1}L_J(n)$ with $n = 0$ representing the lowest energy level of the Stark multiplet [46]. Usually, the CF interaction causes the J manifolds to split into at most $(2J + 1)$ levels for an even number of electrons and $(J + 1/2)$ levels for an odd number of electrons [47]. A special case arises for Eu^{3+} , which has a 7F_0 ground state and a closely spaced higher-lying state 7F_1 , separated by a few hundred cm^{-1} , corresponding to approximately 10 THz. This small energy gap enables significant CF-induced mixing between these two J levels, modifying the J manifold structure and influencing both spectral features and optical transition probabilities [44]. This mixing influences the spectroscopic properties of the respective REI, but a detailed description is beyond the scope of this work. An extensive overview is given in [48, 49]. Another crucial aspect is that, depending on the site symmetry, the J degeneracy can be partially or even completely lifted. For REIs with an even number of electrons in the trivalent state, also called *non-Kramers ions*, the ion must be placed into a low-symmetry environment, such as the C_1 symmetry, in order to fully lift all degeneracies within the electronic level structure. In the case of an odd number of electrons, the so-called *Kramers ions*, the J manifolds retain at least a twofold degeneracy, which can only be lifted by an external magnetic field.

Hyperfine interaction and Zeeman effect: The hyperfine interaction is particularly relevant for isotopes with non-zero nuclear spin. If a nuclear spin I is present, the additional coupling between electronic and nuclear angular momenta causes each Stark level to split into $(2I + 1)$ hyperfine states. The splitting induced by the hyperfine interaction is on the order of 10 MHz (10^{-3} cm^{-1}), which is about five orders of magnitude smaller than the CF level splittings. Since many naturally occurring isotopes have a

nuclear spin $I \geq 1$, meaning their nuclei exhibit a non-spherical charge distribution, higher-order interactions such as the electric quadrupole interaction will further split the hyperfine levels. The energy spacing introduced between these levels is non-equidistant and determined by the strength of the quadrupole interaction. In the case of Eu^{3+} , the two naturally occurring isotopes, $^{151}\text{Eu}^{3+}$ and $^{153}\text{Eu}^{3+}$, have natural abundances of approximately 47.8 % and 52.2 %, respectively, and both possess a nuclear spin of $I = 5/2$. Due to the electronic ground state being characterized by $J = 0$, the hyperfine splitting purely arises from the electric quadrupole interaction, as there is no contribution from the magnetic dipole interaction. In the presence of an external magnetic field, electronic Zeeman and nuclear Zeeman effects can be observed, removing the degeneracy of the Kramers doublets and the hyperfine levels, respectively. According to [49] and [50], the strengths of these interactions are approximately on the same order of magnitude and can be analyzed using a perturbation approach, which provides a deeper insight into the effective spin Hamiltonian.

The general interaction dynamics and level structure of the $4f^N$ configuration are modeled by the following Hamiltonian [50]:

$$\mathcal{H} = [\mathcal{H}_{FI} + \mathcal{H}_{CF}] + [\mathcal{H}_{HF} + \mathcal{H}_Q + \mathcal{H}_Z + \mathcal{H}_z], \quad (2.1.1)$$

where $\mathcal{H}_{FI}$ is the free-ion Hamiltonian, including Coulomb interaction, spin-orbit coupling, as well as the central field Hamiltonian, and $\mathcal{H}_{CF}$ denotes the CF Hamiltonian. Both Hamiltonians in the first bracket are grouped together, as their contributions dominate the overall interaction. In contrast, the remaining terms in the second bracket, which account for nuclear spin and magnetic field couplings, contribute much less, typically on the order of optical inhomogeneous broadening, ranging from a few kilohertz to a few gigahertz [50]. $\mathcal{H}_{HF}$ represents the hyperfine interaction of the $4f$ electrons with the REI nucleus, $\mathcal{H}_Q$ is the nuclear electric quadrupole interaction, $\mathcal{H}_Z$ is the electronic Zeeman interaction, and $\mathcal{H}_z$ denotes the nuclear Zeeman interaction. A more detailed representation of the individual contributions will be developed in Subsection 2.1.3, following the theoretical chapter presented in the thesis of **Nicholas Lester Jobbitt** [28] and the mathematical derivations outlined by **Liu** and **Macfarlane** [49, 50]. In this regard, it is important to place these theoretical concepts in the context of spectroscopic studies. The foundational work conducted by Dieke *et al.* [47] in 1963 established the first general physical trends across the lanthanide series, which serve as an essential reference tool for further REI-based material studies. The original results were presented in the so-called *Dieke diagram*, showing the energy level structure up to $4 \cdot 10^4 \text{ cm}^{-1}$ for all REI species doped into LaCl_3 , with the exception of the radioactive element promethium (Pm^{3+}), which was included in later work [51]. To conclude, due to the shielding of the $4f$ electrons by the $5s$ and $5p$ orbitals, the CF interaction remains relatively small compared to the more dominant Coulomb and spin-orbit interactions. As a consequence, changes in the host material will only slightly modify the energy level structure. To briefly outline our approach and place it in context, we focus on molecular complexes containing Eu^{3+} ions. By systematically modifying the surrounding molecular ligand fields, we aim to investigate the resulting changes in their spectroscopic properties and prove their potential for implementation in future quantum information applications.

Table 2.1: Summary of selection rules for optical $4f \rightarrow 4f$ transitions [48].

Electric dipole transitions	Magnetic dipole transitions
$ \Delta S = 0$	$\Delta S = 0$
$ \Delta L \leq 6$	$\Delta L = 0$
$ \Delta J \leq 6$ and $ \Delta J = 2, 4, 6$ if $J = 0$	$\Delta J = 0, \pm 1$, but not $0 \leftrightarrow 0$

2.1.2. Selection rules for $4f \rightarrow 4f$ transitions

The optical transitions of REIs, particularly the $4f \rightarrow 4f$ transitions, are governed by several selection rules. In free ions, electric dipole transitions are parity forbidden due to the parity of the $4f$ orbitals, while magnetic dipole transitions are parity allowed with $\Delta J = 0, \pm 1$ (but not $0 \rightarrow 0$). However, in solid-state host materials, the lack of inversion symmetry at the substitutional dopant site can relax these restrictions. In low-symmetry environments, such as the C_1 point group symmetry found in Y_2SiO_5 , CF-induced J -mixing breaks the inversion symmetry, making electric dipole transitions weakly allowed. The specific site symmetry of the host material must be carefully examined to determine which transitions are allowed and how strongly they are induced through CF effects. In general, the lower the symmetry, the more favorable the conditions for electric dipole transitions, as symmetry breaking gives rise to an increase in their intensity. For the lowest possible point group symmetry, C_1 (no symmetry), no transitions are forbidden by the selection rules, and transitions are allowed between all the CF sublevels of two $^{2J+1}L_J$ terms. In the following, the most important selection rules are briefly summarized and represented in Table 2.1 [48, 49].

These selection rules are strictly valid only in the Russell–Saunders LS coupling scheme, where the total spin S and the total orbital angular momentum L are good quantum numbers, and selection rules on S and L apply. However, in heavy atoms, including REIs, strong spin-orbit coupling is described by the *intermediate coupling* regime, where S and L are no longer strictly conserved. In contrast, the total angular momentum J remains a good quantum number in both LS and intermediate coupling, making the selection rule on J more robust.

However, these idealized selection rules are often violated either due to strong spin-orbit coupling in the $4f$ shell, which mixes states with different S and L , or through CF-mixing of J multiplets. As a result, transitions such as $^7F_J \rightarrow ^5D_{J'}{}^2$ in Eu^{3+} ($\Delta S = \pm 1$ and $\Delta L = \pm 1$) have been observed, although they are strictly forbidden according to LS -coupling rules. The selection rule on J can also be relaxed in practice. In experiments, $0 \leftrightarrow 0$, $0 \leftrightarrow 3$, and $0 \leftrightarrow 5$ transitions in Eu^{3+} have been observed, potentially arising from strong CF-induced mixing of the $J = 0$, $J = 3$, or $J = 5$ levels with other states, and these transitions possess very weak intensities [48, 49]. In addition, the observation of the

² J and J' denote two different multiplets.

$^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition serves as a clear indication that the Eu^{3+} ion occupies a site with reduced symmetry, such as C_n , C_{nv} , or C_s , where electric dipole transitions between states of the same J become weakly allowed (low intensities) due to CF effects [48].

2.1.3. Crystal field theory: a brief overview

The primary goal of this subsection is to outline a coherent summary of the effective Hamiltonian, aimed at both understanding the modeling of the electronic energy level structure of REIs in solid-state materials and providing a theoretical understanding of the various electronic interactions, which may contribute to interpreting the behavior and spectroscopic studies of newly synthesized molecular complexes. The general theoretical framework is based on two well-established theories, comprising the quantum theory of atomic spectroscopy and the point group theory, which determine the free-ion energy level structures and CF splittings with regard to the symmetry properties of the crystal lattices, respectively. The effect of hyperfine interactions is treated as a perturbation of the electronic energy levels. Their impact on the individual splittings is evaluated on the same basis as the CF interaction. In order to obtain possible solutions to the Hamiltonian, CF modeling utilizes an empirical approach in which the electronic energy levels are determined by diagonalizing the effective Hamiltonian operator using free-ion wavefunctions as the basis. The model parameters of the effective operators can be optimized by fitting the calculated energy levels to the provided experimental data. Detailed theoretical foundations related to mathematical tensor operations and the theory of angular momentum coupling are required for the calculation of the electronic energy level structures of REIs and can be found in the works of **Judd**, **Weissbluth**, and **Cowan** [52, 53, 54]. As stated in the previous subsection, we will introduce the main components of the effective Hamiltonian following the mathematical derivations of **Liu** and **Macfarlane** [49, 50], which are required for modeling the $4f^N$ configuration of REI-based systems [28].

2.1.3.1. Free-ion Hamiltonian

The central field approximation is a conventional starting point to approach an N -electron atomic system. The relativistic Hamiltonian for such an N -electron atom with atomic number Z in free space and in the absence of external fields is composed of the following terms [28, 49]:

$$\mathcal{H} = \sum_{i=1}^N \left[\underbrace{\frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i}}_{\mathcal{H}_O} + \underbrace{\xi(r_i)(s \cdot l)_i}_{\mathcal{H}_{SO}} \right] + \underbrace{\sum_{i < j}^N \frac{e^2}{r_{ij}}}_{\mathcal{H}_C}. \quad (2.1.2)$$

The first contribution of $\mathcal{H}_O$ denotes the kinetic energy of the i th electron with mass m , while the second part represents the Coulomb potential energy of the electron introduced by the field of the nucleus at a radial distance of r_i . The second contribution indicates the spin-orbit interaction $\mathcal{H}_{SO}$, which involves magnetic dipole–dipole interactions between the spin s and the orbital angular momentum l of the electron. The spin-orbit constant $\xi(r_i)$ represents a function depending on r_i . The final contribution, $\mathcal{H}_C$, describes Coulomb repulsion between pairs of electrons which are separated by a distance of r_{ij} . Since more than one electron is considered in this system, an exact solution of the Schrödinger equation is not possible, as methods of separation of variables are not applicable due to coupled values in the spin-orbit interaction. However, the common approach used to find a quantum-mechanical solution is based on the central field approximation, where each electron is considered to move independently of the others in the field of the nucleus and is subjected to a central field which arises from the spherically averaged potential fields of all the other electrons. As a consequence, the first contribution in Equation 2.1.2 is replaced by the following expression of the central field approximation [28, 49]:

$$\mathcal{H}'_O = \sum_{i=1}^N \left[\frac{-\hbar^2}{2m} \nabla_i^2 + U(r_i) \right], \quad (2.1.3)$$

with

$$\sum_{i=1}^N U(r_i) = - \sum_{i=1}^N \frac{Ze^2}{r_i} + \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle. \quad (2.1.4)$$

The second term in Equation 2.1.4 represents the spherically averaged repulsion of the electrons and is therefore independent of the angular coordinates. The concept of this approximation is based on the hydrogen atom, where a single electron is exposed to a central potential. While Equation 2.1.4 introduces the spherically symmetric contributions of the Coulomb electron repulsion, the remaining non-spherical part of the Coulomb repulsion is small enough to be incorporated as a perturbation to the central field defined by the following Coulomb perturbation Hamiltonian [28]:

$$\mathcal{H}_C = \sum_{i<j}^N \frac{e^2}{r_{ij}} - \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle. \quad (2.1.5)$$

Similarly, the spin-orbit interaction is sufficiently small to be treated as a perturbative correction to the central field Hamiltonian and thus can be described by the spin-orbit perturbation Hamiltonian given below [28]:

$$\mathcal{H}_{SO} = \sum_{i=1}^N \xi(r_i) (s \cdot l)_i, \quad (2.1.6)$$

and when the orbital and spin angular momenta of the individual electrons are summed up:

$$L = \sum_{i=1}^N l_i \quad \text{and} \quad S = \sum_{i=1}^N s_i, \quad (2.1.7)$$

the total angular momentum of the LS coupling scheme is given by:

$$J = L + S. \quad (2.1.8)$$

By redefining Equation 2.1.2 using Equations 2.1.3, 2.1.5, and 2.1.6, the modified Hamiltonian is of the form [28]:

$$\mathcal{H} = \mathcal{H}'_O + \mathcal{H}_C + \mathcal{H}_{SO}, \quad (2.1.9)$$

with $\mathcal{H}'_O$ describing the main contributions of the system, while $\mathcal{H}_C$ and $\mathcal{H}_{SO}$ act as perturbations to the central field. This analytical framework enables the systematic solution of the problem and has proven valuable for classifying and calculating energy levels of REIs, as demonstrated by **Wybourne** and **Judd** [41, 52].

2.1.3.2. Crystal-field Hamiltonian

When a REI is introduced into a solid-state host, such as Y_2SiO_5 or Y_2O_3 , the spherical symmetry of the free-ion Hamiltonian is broken due to the electrostatic potential of the surrounding lattice. This local CF lifts the degeneracy of the $(2J + 1)$ electronic states and causes a splitting of the free-ion energy levels. The strength of this splitting is governed by the symmetry of the substitution site in the host material.

For lanthanides, the CF interaction is generally weaker than the Coulomb and spin-orbit interactions and can therefore be considered as a perturbation to the free-ion Hamiltonian. Following the formalism of Wybourne, the CF Hamiltonian is written as [28, 41]:

$$\mathcal{H}_{CF} = \sum_{k,q,i} B_q^k C_q^{(k)}(i), \quad (2.1.10)$$

where the sum runs over all $4f^N$ electrons indexed with i , with B_q^k denoting the CF parameters and $C_q^{(k)}$ representing the spherical tensor operators. The allowed values for k and q are determined by the local symmetry of the crystal site. In the case of the C_1 site symmetry of Y_2SiO_5 , $k = 2, 4, 6$ and $|q| \leq k$, resulting in 27 independent parameters that must be extracted from experimental data. In contrast, higher-symmetry host environments reduce the number of non-zero CF parameters, which simplifies the modeling of the electronic structure [28].

2.1.3.3. Zeeman interactions

In the preceding subsections, the primary interactions that govern the energy level structure of REIs in crystalline host materials have been introduced, including the Coulomb interaction ($\sim 10^4 \text{ cm}^{-1}$ or $\sim 300 \text{ THz}$), the spin-orbit interaction ($\sim 10^3 \text{ cm}^{-1}$ or $\sim 30 \text{ THz}$), and the CF interaction ($\sim 10^2 \text{ cm}^{-1}$ or $\sim 3 \text{ THz}$). The magnetic Zeeman interaction appears at even finer energy scales and results in an additional splitting

of the electronic levels when an external magnetic field is applied. This interaction typically causes level shifts on the order of a few hundred gigahertz ($\sim 10^1 \text{ cm}^{-1}$ or $\sim 300 \text{ GHz}$), lifting the degeneracy of Kramers doublets. The electronic Zeeman effect describes the coupling of the orbital and spin angular momentum of each electron to the external magnetic field. Following the formulation by Wybourne, the corresponding Hamiltonian is given by the expression [28, 41]:

$$\mathcal{H}_Z = \mu_B \sum_i^N \mathbf{B} \cdot (l_i + 2s_i), \quad (2.1.11)$$

where μ_B represents the Bohr magneton, $\mathbf{B}$ the external magnetic field, and l_i as well as s_i are the orbital and spin angular momenta of the i th electron, respectively. Within a single state, where orbital, spin, and total angular momentum (J) are fixed, the Zeeman Hamiltonian can be described as follows [50]:

$$\mathcal{H}_Z = g_J \mu_B \mathbf{B} \cdot \mathbf{J}, \quad (2.1.12)$$

with g_J as the Landé g -factor:

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}. \quad (2.1.13)$$

The Zeeman effect is a key component in manipulating electron spin and hyperfine levels for ensemble spectroscopy, in order to improve coherence properties of REI-based material systems. In addition, the nuclear Zeeman effect can occur, when a nuclear spin is coupled to an external magnetic field. This interaction is determined by the Hamiltonian [28]:

$$\mathcal{H}_z = -\frac{\mu_N \beta_N}{I} \mathbf{B} \cdot \mathbf{I}, \quad (2.1.14)$$

where μ_N indicates the nuclear magneton, β_N the nuclear magnetic dipole moment, $\mathbf{B}$ is the applied magnetic field, and $\mathbf{I}$ the nuclear spin operator. Compared to the electronic Zeeman interaction, the nuclear Zeeman interaction is significantly weaker and often negligible for Kramers ions with unpaired electrons. However, in the case of non-Kramers ions (e.g., Eu^{3+}), where the electronic Zeeman effect is absent due to the lack of an electronic magnetic moment, the nuclear Zeeman effect becomes relevant and contributes to the energy level structure (ZEFOZ technique) [28].

2.1.3.4. Nuclear interactions

The hyperfine and nuclear quadrupole interactions constitute the smallest contributions to the energy level splittings, which are on the order of a few gigahertz ($\sim 10^{-1} \text{ cm}^{-1}$ or $\sim 3 \text{ GHz}$), but in some cases as low as a few megahertz ($\sim 10^{-4} \text{ cm}^{-1}$ or $\sim 3 \text{ MHz}$). These interactions play a crucial role in defining the fine structure of electronic states in REI isotopes with non-zero nuclear spin. The hyperfine interaction arises from the coupling

between the magnetic dipole moment of the nucleus and the magnetic field produced by the orbital and spin angular momenta of the electron. As a consequence, each CF level is split into $(2I + 1)$ hyperfine sublevels, where I represents the nuclear spin. According to Judd, the hyperfine Hamiltonian is described by the following expression [28, 52]:

$$\mathcal{H}_{HF} = 2\mu_B \left[\frac{\boldsymbol{\mu} \cdot \mathbf{l}}{r^3} - \frac{\boldsymbol{\mu} \cdot \mathbf{s}}{r^3} + \frac{3(\boldsymbol{\mu} \cdot \mathbf{r})(\mathbf{s} \cdot \mathbf{r})}{r^5} + \frac{8\pi}{3} \delta(r) \cdot \boldsymbol{\mu} \cdot \mathbf{s} \right], \quad (2.1.15)$$

with $\mathbf{r}$ as the position vector of the electron and $\boldsymbol{\mu} = g_I \mu_N \mathbf{I}$ as the nuclear magnetic moment operator, where g_I denotes the nuclear g -factor and μ_N the nuclear magneton. The terms in the Hamiltonian represent, respectively, the orbital interaction (first term), the spin-dipolar interaction (second and third terms), and the Fermi contact interaction (fourth term), which is relevant for orbitals with non-zero electron density at the nucleus, in particular s orbitals [28, 52]. The nuclear quadrupole interaction describes another significant contribution to the hyperfine structure, especially for REI isotopes with nuclear spin $I \geq 1$, originating from a non-spherical charge distribution of the nucleus, typically due to unpaired nucleons. The resulting nuclear electric quadrupole moment interacts with the electric field gradient induced by the electrons surrounding the nucleus. The nuclear quadrupole Hamiltonian as formulated by Wybourne, is expressed as [28, 41]:

$$\mathcal{H}_Q = -e^2 \int_{\tau_e} \int_{\tau_n} \rho(r_e) \rho(r_n) \frac{r_n^2}{r_e^3} \left(C_e^{(2)} \cdot C_n^{(2)} \right) d\tau_e d\tau_n, \quad (2.1.16)$$

where $e\rho(r_e)$ and $e\rho(r_n)$ indicate the electron and nuclear charge densities, respectively, while r_e and r_n are the distances of the electrons and the nucleons from the center of the nucleus. $C_e^{(2)}$ and $C_n^{(2)}$ represent second-rank spherical tensor operators, which describe the angular distributions and are related to spherical harmonics. In conclusion, this interaction further lifts the degeneracy of the hyperfine levels [28, 41]. Another more practical approach for modeling the magnetic and hyperfine structure of specific states more accurately is based on using a spin Hamiltonian, which only applies to a single electronic state. According to Macfarlane, the spin Hamiltonian for Kramers ions is given as [28, 50]:

$$\mathcal{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I} - g_I \mu_N \mathbf{B} \cdot \mathbf{I}, \quad (2.1.17)$$

with μ_B as the Bohr magneton, $\mathbf{B}$ as the external magnetic field, $\mathbf{g}$ as the magnetic g tensor, $\mathbf{A}$ as the hyperfine tensor and $\mathbf{Q}$ as the electric quadrupole tensor. $\mathbf{S}$ and $\mathbf{I}$ are the electronic and nuclear spin operators, respectively. g_I represents the nuclear g -factor, while μ_N denotes the nuclear magneton. For non-Kramers ions, the spin Hamiltonian is described by the formulation used by Longdell *et al.* [55]:

$$\mathcal{H} = \mathbf{B} \cdot \mathbf{M} \cdot \mathbf{I} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I}. \quad (2.1.18)$$

In this case, the first term indicates the nuclear Zeeman interaction and the second term represents the nuclear quadrupole interaction, whereas $\mathbf{M}$ and $\mathbf{Q}$ are the effective Zeeman and quadrupole tensors, respectively [28, 55]. All contributions are included here for completeness but will not be explicitly derived or discussed further in this work.

2.2. Line broadening mechanisms

Having established a general understanding of the effective Hamiltonian, which is required to describe the energy level structure in REI-based material systems, our focus in this section is on elaborating the broadening mechanisms of optical spectral lines. In experimental measurements, the energy levels of REIs are usually not observed as discrete lines but as broadened spectral features. Nevertheless, individual transitions can exhibit extremely narrow linewidths, often in the kilohertz range, when the ions are subjected to cryogenic temperatures and embedded in low-strain host environments. The broadening effects can be categorized as follows. *Homogeneous broadening* comprises all interactions that affect all REIs in the host material in a uniform manner, while *inhomogeneous broadening* originates from variations in the local environment across different ions within the host material. The measurement and analysis of homogeneous and inhomogeneous linewidths form a central part of this thesis, as they provide key parameters of the material performance and quality in the search for suitable REI-based quantum systems.

2.2.1. Natural linewidth

Before introducing dephasing and broadening mechanisms, we consider the simplest case of an isolated two-level system, which can be modeled as a damped harmonic oscillator to describe the spectral distribution of the optical transition. In this idealized scenario, the electronically excited state relaxes to the ground state via spontaneous emission, resulting in a finite lifetime. This decay process leads to natural broadening of the transition, yielding a characteristic Lorentzian line shape in the frequency domain:

$$L(\omega) = \frac{\Gamma/2\pi}{(\omega - \omega_0)^2 + (\Gamma/2)^2}, \quad (2.2.1)$$

where ω indicates the frequency, ω_0 the resonance frequency of the oscillator or the transition when no damping is present, and Γ the corresponding spectral width, usually referred to as the full width at half maximum (FWHM) linewidth. In the absence of external perturbations, this linewidth is known as the *natural linewidth* Γ_0 , and represents the fundamental limit to the sharpness of an optical transition. It is directly related to the excited-state lifetime T_1 via the following expression [56]:

$$\Gamma_0 = \frac{1}{2\pi T_1}. \quad (2.2.2)$$

The excited-state lifetime of the corresponding material system is highly dependent on the embedded environment and the local interactions, which can induce relaxation processes into additional available electronic states. Material platforms integrated into optical cavities can exhibit an enhancement of the spontaneous emission rate via the Purcell effect, which results in a shortening of the excited-state lifetime. Such effects are advantageous in coherent cavity-mediated spectroscopy [34, 57].

2.2.2. Homogeneous line broadening

The homogeneous linewidths of optical transitions in REI-doped solid-state materials are governed by a variety of dynamical processes that persist even at cryogenic temperatures. The analysis of these processes can provide deep insights into the different interactions occurring between REIs and the local environment. In general, homogeneous broadening results from mechanisms that affect all REIs across the host lattice in the same way. Any process that induces a real transition from either the initial or final electronic state of an individual optical transition will influence the homogeneous linewidth. The primary processes are outlined and described in the following [49]:

1. **Excited-state decay:** Emission of photons (radiative process) via the decay of an ion from the excited state to the ground state or a lower state.
2. **Phonon interaction:** On one hand, thermally available phonon populations (non-radiative process) can interact with an ion in the ground state or excited state, inducing real transitions between CF levels within a J manifold. On the other hand, virtual two-phonon processes cause phase noise, disrupting the transition dipoles and thus leading to additional homogeneous broadening.
3. **Ion and nuclear spin interactions:** Transitions among electron and nuclear spin states can occur within the ion or its environment, while the dynamics of the nearest neighbors can modulate the optical transition frequency, which contributes to the overall dephasing.

Taking all these mechanisms into account, the homogeneous linewidth Γ_h is determined as the inverse of the dephasing or coherence time T_2 :

$$\Gamma_h = \frac{1}{\pi T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}, \quad (2.2.3)$$

where T_1 denotes the excited-state or population lifetime, and T_2^* corresponds to the relaxation time of pure dephasing processes. The excited-state lifetime includes contributions from radiative and non-radiative decays. Optical transitions within the $4f^N$ configuration are typically parity- and in some cases also spin-forbidden, meaning they occur between states of the same parity and without a spin flip. However, in practice, this forbidden character is partially lifted due to several effects introduced by the host material, such as mixing of the CF levels, which modify and relax the strict selection rules. As a consequence, the $4f \rightarrow 4f$ transitions are very weak and long-lived, resulting in radiative-decay-dominated excited-state lifetimes on the millisecond scale. In terms of homogeneous linewidths, this corresponds to very narrow linewidths in the range of a few kilohertz down to the sub-kilohertz regime. In the absence of pure dephasing, the homogeneous linewidth is determined solely by its natural limit, as stated above, and is typically referred to as the *lifetime-limited linewidth*.

At room temperature, for most low-defect crystalline materials, homogeneous broadening is typically the dominant contribution to the optical transition due to an increased phonon population. In contrast, at low temperatures, the phonon occupation decreases, and inhomogeneous broadening becomes more pronounced. Nevertheless, there are many advanced spectroscopic techniques to probe the homogeneous linewidth within the inhomogeneous broadening and to extract details of the underlying dynamical broadening processes. These spectroscopic methods are presented in Chapter 4. A notable measurement was performed by Equall *et al.* [18], who observed a very narrow and lifetime-limited homogeneous linewidth of 122 Hz in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ at cryogenic temperatures using two-pulse photon echo measurements (see Section 4.3). In the following, we distinguish between three principal types of interactions that affect the homogeneous linewidth and lead to decoherence: ion–phonon interactions, ion–ion interactions, and interactions with surrounding nuclear spins.

2.2.2.1. Ion–phonon interactions and temperature dependence

Observing the different interactions and their temperature dependencies can provide insights into the structural order of the material and the local environment of the embedded ions. For this reason, amorphous structures exhibit different spectroscopic properties compared to well-crystallized materials, for example, homogeneous linewidths can be several orders of magnitude broader. Nevertheless, the underlying physical processes remain the same across all material types.

One major contribution to homogeneous broadening in solid-state materials consists of phonon processes [49], particularly at non-cryogenic temperatures. Depending on the energy level splittings within the ground and excited CF multiplets, different phonon-related processes can occur. The simplest phonon mechanism is a direct or resonant one-phonon-induced transition (phonon absorption or emission), occurring between two crystal levels either in the ground or excited state manifold, as illustrated in Figure 2.4(a), while a distorted real crystal lattice caused by impurities and defects, leading to local strain and affecting phonon interactions, is shown in Figure 2.4(b). As each transition involves an excited CF level, the corresponding ion relaxes via spontaneous emission of a phonon with a rate $1/T_{1d}$, contributing to the homogeneous broadening:

$$\Gamma_{h,d} = \frac{(n+1)}{2\pi T_{1d}}, \quad (2.2.4)$$

with n denoting the occupation number of the phonons with frequency ω , whose energy is directly related to the involved energy level separation by $\Delta = \hbar\omega$. If additional higher-lying levels in the manifold participate in the transition, then all phonon processes from other energy levels in the manifold that couple to this level must be considered, each contributing additively to the homogeneous linewidth. In the case of the lowest

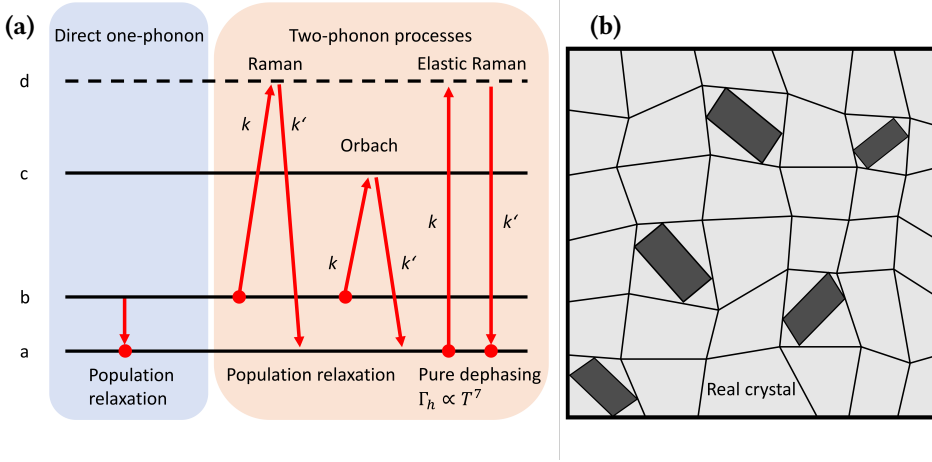


Figure 2.4: Phonon-induced dephasing mechanisms and lattice distortion in real crystals.

(a) The left diagram illustrates phonon-induced dephasing mechanisms between CF levels labeled as a , b , and c . The depicted processes include a direct one-phonon relaxation (blue), a two-phonon Raman process via a virtual state d , an Orbach process involving real intermediate states, and a two-phonon pure dephasing process likewise mediated via a virtual state d (all three processes highlighted in red). Unlike the other mechanisms, pure dephasing does not involve population transfer but results in a loss of coherence due to local field fluctuations. In particular, the Raman-type processes lead to a broadening of the homogeneous linewidth with a characteristic $\propto T^7$ temperature dependence for non-Kramers ions ($\propto T^9$ for Kramers ions). Panel (a) adapted from [49]. (b) Schematic of a distorted real crystal lattice caused by substitutional or interstitial atoms and impurities, demonstrating the emergence of local strain and disorder. These effects can alter phonon interactions and thus enhance dephasing mechanisms through increased environmental fluctuations.

level of a CF manifold, only stimulated direct phonon processes can occur, resulting in the following contribution to the homogeneous broadening:

$$\Gamma_{h,d} = \frac{(n)}{2\pi T_{1d}}. \quad (2.2.5)$$

The phonon occupation number increases with temperature, and the phonon relaxation rate $1/T_{1d}$ grows with the cube of the phonon frequency ($\propto \omega^3$) in the Debye approximation ($k_B T \ll k_B T_{\text{Debye}}$) [58]. As a consequence, optical transitions that originate from higher-lying states in a CF manifold (emission or absorption) exhibit more substantial broadening than those involving the ground state, motivating the use of absolute ground-state transitions of the material system (e.g., for Eu^{3+} , ${}^7F_0 \rightarrow {}^5D_0$) in coherent ensemble spectroscopy [49].

Beyond single-phonon effects, higher-order processes involving two or more phonons can further contribute to dephasing. As shown in Figure 2.4(a), two distinct non-resonant processes mediated by virtual states, namely the two-phonon Raman process and an

elastic Raman process corresponding to pure dephasing, as well as one resonant Orbach process involving real intermediate states, can be identified. The two-phonon Raman rate is described by the following expression [49]:

$$1/T_{2R}^* = \int M^2 n(\omega) [n(\omega) + 1] \rho(\omega)^2 d\omega, \quad (2.2.6)$$

where M denotes the two-phonon electron-phonon matrix element and $\rho(\omega)$ is the phonon density of states. The two-phonon Raman processes contribute significantly to the homogeneous linewidth of REIs at both low and high temperatures. In the low-temperature regime, where direct one-phonon processes from the lowest levels in the ground and excited state manifolds are suppressed due to low phonon occupation numbers, the two-phonon Raman mechanism can constitute the dominant contribution to the homogeneous linewidth. The integration of Equation 2.2.6 over all phonon modes for low temperatures ($T \ll T_{\text{Debye}}$) results in a $\propto T^7$ temperature dependence of the homogeneous linewidth for non-Kramers ions ($\propto T^9$ for Kramers ions) [57, 59]:

$$\Gamma_{2R} \propto \bar{\alpha}_{2R} \cdot T^7. \quad (2.2.7)$$

Due to its complexity, the full coefficient $\bar{\alpha}_{2R}$ has not been included here and is available in the referenced literature [59]. In Eu^{3+} -based materials, the coherent ${}^7F_0 \rightarrow {}^5D_0$ optical transition is particularly sensitive to dephasing induced by two-phonon Raman processes. This is attributed to the singlet nature of both ground and excited states, as well as their large energy separation, which suppress direct single-phonon processes and enhances Raman contributions. At elevated temperatures, these two-phonon processes remain dominant, as they involve all phonon modes, yielding a $\propto T^2$ temperature dependence of the homogeneous linewidth. In contrast, resonant Orbach processes, facilitated by real intermediate CF levels, exhibit an exponential temperature dependence and often represent the primary limitation to electron spin coherence times [49].

For disordered and amorphous solid-state systems doped with molecules or ions, the temperature dependence of the homogeneous linewidth includes additional effects and is expressed for low temperatures by the following equation [60, 61]:

$$\Gamma_h(T) = \Gamma_0 + b \cdot T^{\alpha_{\text{TLS}}} + \Delta\Gamma_{\text{LFM}}(T), \quad (2.2.8)$$

where $b \cdot T^{\alpha_{\text{TLS}}}$ describes the contribution of interactions with tunneling two-level systems (TLSs), with an exponent α_{TLS} close to unity, and $\Delta\Gamma_{\text{LFM}}(T)$ denotes the broadening due to dephasing by phonons and quasi-localized low-frequency vibrational modes (LFMs). In crystalline solids, LFMs often emerge near impurities or point defects and are weakly coupled to the surrounding lattice. Because of this coupling, these modes are not strictly confined to the defect center but are instead *quasi-localized*, meaning their vibrational amplitude extends into the surrounding region. When the crystal is doped uniformly with a single type of impurity, the resulting LFMs tend to have similar properties, and their average behavior can be used to describe the resulting dynamics and their contribution to dephasing processes [60].

In contrast, in disordered or amorphous materials, LFMs are inherent and widespread due to the structural heterogeneity of the matrix. Here the modes originate from the irregular local environments, which act as point defects, and feature a wide distribution in their frequency and spatial characteristics. These modes can interact with optically addressed ions and thus contribute to decoherence, particularly at low temperatures. The contribution of LFMs is of the form [60]:

$$\Delta\Gamma_{\text{LFM}}^i(T) = \sum_j w^{ij} \frac{\exp(-h\nu^j/k_B T)}{[1 - \exp(-h\nu^j/k_B T)]^2}, \quad (2.2.9)$$

with i as the index of a particle or ion interacting with a vibrational mode of index j and frequency $\nu^j = \Delta E^j/h$, and w^{ij} are the corresponding coupling constants.

The contribution from TLSs is nearly linear in temperature and, like LFMs, represents a prevalent source of decoherence. In disordered or amorphous materials, the embedded ions do not occupy fixed lattice positions due to the absence of long-range order. Instead, they are surrounded by numerous local energy minima, and at low temperatures, they can tunnel between two nearly degenerate configurations separated by an energy barrier. This tunneling induces random energy shifts in the local environment, causing decoherence. In crystalline systems, similar effects may arise from structural imperfections [62, 63].

As a conclusion, at temperatures above approximately 10 K to 20 K, homogeneous broadening is predominantly governed by two-phonon Raman processes, whereas at lower temperatures, additional broadening contributions such as TLSs and quasi-localized LFMs become more significant [64]. Therefore, further cooling to sub-kelvin or even millikelvin temperatures remains a crucial strategy to mitigate these dephasing mechanisms and improve both the optical and spin coherence properties of REI systems.

2.2.2.2. Ion-ion interactions

The optical transition frequency of an individual ion can be affected by dynamic interactions with the local environment. Any time-dependent perturbation can shift the transition frequency, leading to dephasing of the transition dipole moment and consequently to a broadening of the homogeneous linewidth. This process is referred to as *spectral diffusion* and involves electron spin–spin interactions, electron–nuclear spin interactions, excitation-induced frequency shifts, and energy transfer processes. The induced frequency shift Δf_{ij} of electric dipole–dipole interactions is described by the following equation [64, 65]:

$$\Delta f_{ij} = \frac{\mu^2}{4\pi\epsilon\epsilon_0 h r_{ij}^3} [\hat{\mu}_i \hat{\mu}_j - 3(\hat{\mu}_i \hat{r}_{ij})(\hat{\mu}_j \hat{r}_{ij})], \quad (2.2.10)$$

where μ represents the electric dipole moment of the ion, h the Planck's constant, κ_0 the vacuum permittivity, ϵ the dielectric constant of the host material, and r_{ij} the

separation between ion i and ion j . When a subset of ions in the ensemble is optically excited, their altered dipole moments induce changes in the local electric field, which in turn shift the resonance frequencies of nearby, unexcited ions. This effect, known as *instantaneous spectral diffusion (ISD)*, arises from long-range dipole–dipole interactions and occurs on ultrafast timescales during the excitation process, effectively leading to a broadened spectral line of the probed transition [65]. As a consequence, dense ensembles are particularly susceptible to ISD processes and this effect must be considered when evaluating coherence properties or designing high-fidelity gate operations in REI-based quantum systems [33, 57].

Kramers ions, which possess unpaired electrons, experience strong magnetic dipole–dipole interactions between electronic spins, which dominate dephasing even at relatively low doping concentrations. Mutual spin flip-flop processes, originating either from the surrounding environment or from direct interactions with the ion itself, introduce frequency fluctuations of the optical transition on the order of several megahertz. For this reason, Kramers ions require extremely dilute samples ($\ll 10$ ppm) in order to observe narrow homogeneous linewidths. Nevertheless, large external magnetic fields can be applied to freeze out the electron spins at cryogenic temperatures, enabling long optical coherence times. In contrast, non-Kramers ions, such as Eu^{3+} , which lack unpaired electrons, exhibit no electron magnetic moments to first order and thus experience much weaker magnetic interactions. This allows for the realization of promising optical coherence properties [49].

2.2.2.3. Nuclear spin interactions

Dynamical processes induced by the local nuclear environment can significantly affect the homogeneous linewidth, particularly when phonon-induced dephasing is suppressed at cryogenic temperatures. As different nuclear spin configurations are present, the resulting time-dependent local magnetic fields interact with the electron–nuclear states of the ion. Subsequent spin flip–flops of the surrounding nuclei induce fluctuations in these magnetic fields, which modulate the transition frequencies of the corresponding optical centers. The interaction generates a frequency shift $\Delta\nu$, described by the following expression [49]:

$$\Delta\nu = \frac{\mu_e \mu_n}{r^3}, \quad (2.2.11)$$

with μ_e denoting the electron magnetic moment, μ_n the nuclear magnetic moment, and r the distance between the optical center and the nearby nuclear spin. For typical nearest-neighbor distances of $\sim 3 \text{ \AA}$, this interaction leads to frequency shifts on the order of several megahertz. Such couplings are commonly referred to as *superhyperfine interactions*, as they describe the interaction between the electron spin of the ion and the nuclear spins of the surrounding host lattice. In non-Kramers ions, where the electronic

magnetic moment vanishes to first order, nuclear spin–spin interactions between the ion and the surrounding host nuclei can also occur. However, these interactions are typically much weaker than electron-mediated interactions and therefore contribute less significantly to the overall dephasing. Nevertheless, the contribution of individual nuclear spins is highly non-uniform. An additional important aspect is the so-called *frozen core effect*, which refers to a spatial region around the dopant ion in which nuclear spin dynamics are strongly inhibited. This suppression occurs because the electronic magnetic moment of the dopant ion generates a strong local magnetic field that shifts the energy levels of surrounding nuclei asymmetrically. As a result, mutual spin flip–flop processes between these nearby nuclei become energetically unfavorable, so that their flip rates are drastically reduced. The nuclear spins within the frozen core can be considered a quasi-static field, which evolves only very slowly on typical experimental timescales, while occasional changes can induce comparatively large frequency shifts and thus contribute to the dephasing. In contrast, the nuclear spins beyond the frozen core experience weaker local fields and can undergo faster spin flip–flop processes. For this reason, their individual contributions to the frequency shift are small, but their significantly higher spin flip rates can effectively increase the dephasing through spectral diffusion. In conclusion, the frozen core serves as a buffer region that shields the dopant ion from fast local magnetic fluctuations induced by neighboring nuclei [20, 49].

2.2.2.4. Power broadening

An important effect that can occur during measurements and must be taken into account is *power broadening*, which is caused by high power levels of the laser excitation light and leads to broadening of the homogeneous linewidth. Power broadening is determined by the following relation [56]:

$$\Gamma_{\text{eff}} = \Gamma_0 \sqrt{1 + \left(\frac{\Omega_R}{\Gamma_0} \right)^2}, \quad (2.2.12)$$

where Γ_{eff} denotes the power broadened effective linewidth, Γ_0 the natural homogeneous linewidth, Ω_R the Rabi frequency ($\Omega_R = \mu E / \hbar$), which scales with the square root of the excitation power. In order to quantify the contribution of power broadening, measurements are performed at various excitation powers, and the resulting effective linewidths are analyzed. Once a saturation trend in the linewidth is observed as a function of laser power, the data can be fitted accordingly, allowing the extraction of the intrinsic homogeneous linewidth by extrapolating to zero excitation power [56, 57].

2.2.3. Inhomogeneous line broadening

Although macroscopic solid-state materials have a defined crystal lattice structure, a real crystal exhibits irregularities, such as disorder and defects. For this reason, each ion doped into a solid experiences a slightly different local environment, leading to a statistical distribution of optical transition frequencies, which overlap and form an inhomogeneously broadened spectral feature [49], as shown in Figure 2.5(a). The shift in the transition frequency is primarily influenced by strain, lattice defects, including vacancies, interstitials, and impurities, as well as by charge compensation effects and local electric or magnetic fields produced by nearby ions. All of these contributions are inherent to real crystalline materials. Apart from solid-state systems, such statistical distributions are also observed in gases, where the inhomogeneous broadening is denoted as *Doppler broadening*, since the spectral lines are governed by the *Doppler effect* [56, 57]. In both cases, the resulting spectral line is broadened in shape, but the line profile depends on the nature and distribution of these perturbations. For a Doppler gas, the inhomogeneous line is usually fitted by a Gaussian function because there is a Gaussian distribution of the velocities of gas particles. For REI ensembles embedded in crystals, both Gaussian and Lorentzian line shapes are possible, as shown in theoretical studies by Orth *et al.* [66]. However, the Lorentzian shape is in most cases the most suitable model to fit the observed spectral feature [67]. According to Stoneham *et al.* [68], the application of the Lorentzian model can be explained by a statistical approach, which assumes a low defect concentration to avoid correlations between them, and that these defects induce a linear contribution to the energy perturbation. The results of the statistical analysis reveal a Lorentzian profile for the inhomogeneous broadening [62, 68].

To place this in the context of our work, we focus on REI (or specifically Eu^{3+}) ensembles containing millions of ions, which correspond to a doping concentration of 100 % in molecular samples studied within this thesis in Chapter 4. Figure 2.5(b) illustrates a representative measurement of the inhomogeneous linewidth fitted with a Lorentzian function. As stated above, the inhomogeneous line comprises a distribution of optical transition frequencies, which is equivalent to a series of homogeneous lines. In the case of large REI ensembles, it does not necessarily mean that each homogeneous line represents a single ion. Therefore, large ensembles can be divided into *classes* and *subclasses* of ions, where each class is characterized by a common optical transition frequency and homogeneous linewidth. The superposition of all classes results in the characteristic inhomogeneous line of the ensemble. However, it is important to note that the homogeneous and inhomogeneous linewidths are not directly correlated with each other, meaning that a narrow inhomogeneous linewidth does not inherently imply a narrow homogeneous linewidth and vice versa [57].

Due to the large variety of available host materials, extensive spectroscopic investigations are required to fully characterize a new quantum emitter system. Each material can possess different defects or environmental influences compared to already known

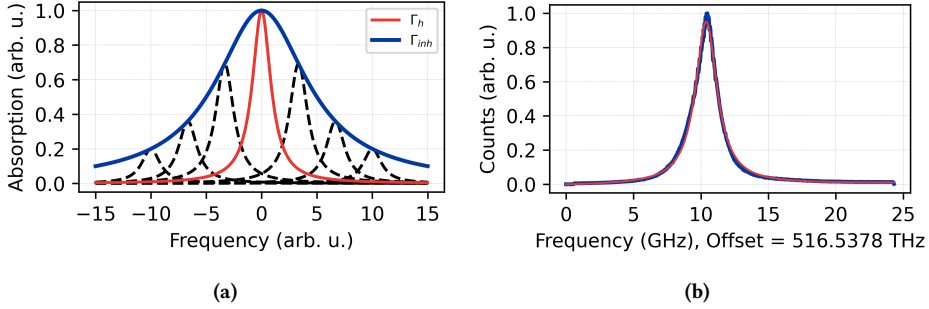


Figure 2.5: Representation of the inhomogeneous linewidth. (a) The inhomogeneous linewidth (blue) of an REI ensemble is illustrated as a broad envelope composed of numerous narrow homogeneous lines (ratios of $\Gamma_{inh}/\Gamma_h \sim 10^4$ to 10^7), each corresponding to subclasses of ions experiencing slightly different local environments, resulting in shifted transition frequencies. One representative homogeneous line is highlighted in red for clarity, with its width exaggerated relative to the inhomogeneous line for illustrative purposes. (b) Experimental measurement of an inhomogeneously broadened line from a self-synthesized Eu^{3+} -doped molecular complex. Such measurements enable comparison across different material systems and provide insights into the degree of structural order.

material structures [49]. Some crystalline materials can exhibit certain defects around the optical center in a regular manner, resulting in narrow homogeneous linewidths, such that distinct lines can be resolved and selectively probed with coherent spectroscopic techniques (see Section 4.2.1). In the case of substituting a host ion with a different charge, for example when a trivalent REI replaces a divalent cation, regular charge gradients result in distinct site perturbations. Highly disordered or amorphous materials exhibit especially large inhomogeneous linewidths because of significant local environmental variations experienced by the optical centers. In nanoscale materials, inhomogeneous broadening can arise from the spatial distribution of REIs. Since many of them will be located near the surface, additional effects, such as surface charges, can be induced. Another notable source of inhomogeneous broadening stems from the statistical distribution of isotopes in neighboring host ions, resulting in isotope-dependent shifts in the hyperfine structure [69, 70]. Although the measurement of the inhomogeneous linewidth does not provide direct information on the coherence properties of the respective REI-based material system, it still serves as a figure of merit for evaluating the material properties, including the uniformity and the structural order of the crystal lattice [57, 71].

Table 2.2: Comparison of key properties of Y_2SiO_5 (site 1) and Y_2O_3 (C_2) as host materials for Eu^{3+} ions. The symmetry site that yielded better results was selected for the comparison. The properties, listed from top to bottom, are: excitation wavelength, frequency, optical lifetime, optical coherence time, hyperfine lifetime, hyperfine coherence time and oscillator strength. Magnetic field strengths are stated in brackets, as some measurement techniques with an external magnetic field were applied (e.g., ZEFOZ) [33, 50, 72, 73].

Property	$\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ (site 1)	$\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ (C_2)
λ_{exc}	579.879 nm	580.88 nm
ν	516.991 THz	516.100 THz
$T_{1,o}$	1.9 ms	860 μs
$T_{2,o}$	2.6 ms ($B = 10$ mT)	1.1 ms
$T_{1,s}$	> 20 d	> 30 h
$T_{2,s}$	≈ 19 ms	≈ 12 ms
$T_{2,s}$ (CPMG + ZEFOZ)	≈ 18 h ($B = 1.35$ T)	-
Oscillator strength	$1.2 \cdot 10^{-8}$	-

2.3. Eu^{3+} -based materials

The choice of a host material plays a critical role in determining both optical and spin characteristics of REI-based systems. The host lattice can introduce dephasing mechanisms, such as phonon interactions and magnetic noise, which limit the coherence times. Therefore, selecting an appropriate host material is essential for enhancing the optical transition properties and the spin stability in the local environment. Among the most studied hosts for Eu^{3+} are *yttrium orthosilicate* ($\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$) and *yttrium oxide* ($\text{Eu}^{3+}:\text{Y}_2\text{O}_3$), with each offering distinct advantages. In the following, the lattice structure and properties of both host crystals are briefly discussed, and the spectroscopic properties of the two emitter systems are summarized in a comparative Table 2.2, serving as a reference for the investigation of new Eu^{3+} -based material systems.

Y_2SiO_5 : Y_2SiO_5 crystals are monoclinic ($a \neq b \neq c$), incorporate eight formula units within the unit cell, and feature two distinct substitutional Y^{3+} sites for REI dopants. The unit cell exhibits C_{2h} symmetry, while both substitutional sites possess C_1 point group symmetry (no symmetry) and are distinguished by their coordination numbers of six (site 1) and seven (site 2), respectively. The crystallographic axes a , b , and c are rotated with respect to the principal axes D_1 , D_2 , and $D_3 = b$, as the crystal is birefringent. Each axis possesses a slightly different refractive index. The major advantage of Y_2SiO_5 crystals lies in their exceptionally quiet local environment, which minimizes magnetic fluctuations. Silicon and oxygen exhibit no nuclear spin, while yttrium (specifically $^{89}\text{Y}^{3+}$) has a nuclear spin of $I = 1/2$. However, its magnetic moment is relatively small ($-0.137\mu_N$, where μ_N denotes the nuclear magneton) [74]. Low magnetic moments reduce magnetic dipole–dipole interactions and suppress spin flip–flop processes of

the host nuclei, which would otherwise degrade the optical and spin coherence of the embedded REIs [28, 33]. Spectroscopic measurements are typically performed on macroscopic bulk crystals.

Y_2O_3 : Y_2O_3 crystallizes in a cubic lattice structure ($a = b = c$) with space group $Ia\bar{3}$. The unit cell is composed of 16 formula units and contains two non-equivalent substitutional Y^{3+} sites for REIs, exhibiting C_2 and S_6 symmetry, respectively, both of which have sixfold coordination [75]. The host environment is similar to that of Y_2SiO_5 , as only the Y^{3+} nuclei contribute to magnetic moments and thus local magnetic field fluctuations. The cubic symmetry provides uniform local magnetic fields. Compared to lower-symmetry hosts (such as monoclinic Y_2SiO_5), this can lead to reduced shielding of the REI dopant from environmental magnetic fluctuations, which may adversely affect the spin and optical properties. Both bulk crystals and nanoparticles of this material have been investigated for their suitability as host systems. Due to their compact geometry, the nanoparticles are especially compatible with open-access fiber-based microcavities. However, the reported spin properties differ from those of the bulk material, indicating additional dephasing mechanisms, which potentially arise from proximal surface charge fluctuations. Nevertheless, the experimentally determined optical characteristics have proven to be promising [46, 57, 64, 72].

2.4. Toward REI-based quantum information applications

In order to realize the physical implementation of quantum information processing, certain fundamental criteria applicable to all quantum computing platforms must be fulfilled to ensure reliable and scalable quantum operations. These criteria were established by **David P. DiVincenzo** [3] in the context of describing and developing quantum computers and quantum communication systems and serve as a general framework to evaluate the feasibility and scalability of implementing any quantum architecture, such as, in our, case REI-based quantum systems.

Within the scope of this thesis, only a small component of the REI-based quantum architecture was investigated, but the fundamental idea will be addressed and put into context in this part of the theoretical discussion. Given the promising properties of REIs, especially their long coherence times and the efficient realization of spin-photon interfaces, they already represent a strong candidate for scalable quantum technologies. This section outlines the general DiVincenzo criteria and places them in the context of the current status of REI research, including the achievements of the SQUARE project consortium.

2.4.1. DiVincenzo criteria for quantum information applications

The fundamental requirements for the realization of quantum computation and communication are summarized in the well-known "*five plus two*" *DiVincenzo criteria* [3]. In the following, these criteria are briefly introduced and discussed in the context of recent advances in REI material systems, particularly highlighting progress achieved within the SQUARE project [33] and other significant contributions provided by the broader REI research community.

1. Scalability of well-characterized qubits: The quantum computing system must have a physical platform containing a collection of many qubits. A qubit is in its simplest form a quantum two-level system that can be represented by states $|0\rangle$ and $|1\rangle$ introduced by the spin states or the ground and excited states of the emitter system. The main difference between a qubit and a bit is that qubits exist in a superposition of these states, meaning that the permitted states of a single qubit are displayed within a two-dimensional complex vector space. In a system with multiple qubits, the combined state is a vector in a 2^n -dimensional complex space. The distinguishable states of an n -qubit system can be *entangled*, meaning mathematically that they cannot be described as independent products of individual qubit states.

A *well-characterized* qubit is one whose physical parameters are accurately known and controlled, so that the qubits behave predictably and can be manipulated with high precision. The key aspects of a well-characterized qubit are as follows:

- Internal Hamiltonian for determining energy eigenstates
- Couplings and interactions with other states, external fields, and neighboring qubits
- Isolation from unwanted states via correct design of the control apparatus
- Quantum error correction (QEC) mechanisms must be capable of detecting and correcting errors arising from leakage to unwanted states or interactions with the environment

Status quo of criteria 1: Applying this criterion to the case of REIs, well-characterized ensemble qubits have been experimentally realized [20, 46, 76, 77]. In general, REI systems offer excellent scalability due to the large ratio ($\sim 10^4$ to 10^7) between the inhomogeneous broadening and the homogeneous linewidth, allowing many ions to be individually addressed within the same node. However, for Eu^{3+} -based systems, unfortunately, the demonstration of single-ion qubits has not yet been achieved. Nevertheless, the overall progress within the REI community has reached the point where multiple coherent control and entanglement of single ions have been demonstrated. As demonstrated by the group of **Professor Andrei Faraon** [78], two $^{171}\text{Yb}^{3+}:\text{YVO}_4$ ions

in remote nanophotonic crystal cavities were utilized to herald bipartite entanglement and probabilistically teleport quantum states between both quantum nodes.

2. Qubit initialization to a simple fiducial state: Before the start of any logical computational step, the qubit register should be reliably initialized to a well-defined state. In addition, QEC schemes require a continuous, fresh supply of qubits in a low-entropy state, such as the $|0\rangle$ state, to function properly. From this aspect, the primary challenge is the speed with which a qubit can be reinitialized to prevent computational delays. If the initialization process is relatively long compared to gate operation times, then additional measures have to be taken into account. A possible solution is the conveyor belt scheme, which proposes to separate the non-initialized qubits from the computation area and reintroduce them back to the system as soon as they are operational again.

Status quo of criteria 2: Qubit initialization schemes in REI systems are now well established for both ensemble-based and single-ion qubit approaches. Optical pumping is used in several spectroscopic methods and can be employed such that a single hyperfine state is initialized. For instance, $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$ and $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ utilize spectral tailoring to prepare a desired ground state before storage operations are initiated [79]. High-fidelity initialization (> 0.95) has been also demonstrated for single REI qubits, in particular single Yb^{3+} ions, coupled to a microcavity [80]. Although REI systems can be reliably brought to a known state, the fidelities still must be optimized to near unity for practical quantum applications.

3. Long coherence times: Decoherence describes the process where a quantum state loses its coherence due to interactions with the environment and the occurrence of classical behavior. Mathematically, decoherence effectively transforms a pure state $|\psi\rangle = a|0\rangle + b|1\rangle$ into a classical mixture $\rho = |a|^2|0\rangle\langle 0| + |b|^2|1\rangle\langle 1|$. The decoherence time represents the timescale over which a qubit remains coherent before interacting with its environment. The required duration must be significantly longer than the time needed to perform a meaningful amount of gate operations or logical operations as well as any error correction. To make the quantum system even fault-tolerant, so that the errors can be corrected faster than they appear, the decoherence times should be between 10^4 up to 10^5 times longer than the time used to carry out single-gate operations. In general, decoherence is a highly system-specific phenomenon, which strongly depends on the host material and the type of quantum emitter, implying that new material systems require precise characterization of their properties, as they may differ drastically from already well-studied and similar quantum systems.

Status quo of criteria 3: REI qubits are well-known for their extremely long coherence times. Applying combined techniques such as ZEFOZ and dynamical decoupling control, REI-doped solid-state materials have achieved record values. In particular, $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ has demonstrated nuclear spin coherence times of several hours at cryogenic temperatures, which have recently been extended to ≈ 18 h in the same material [20, 21], but only

at millikelvin temperatures. This reported coherence time is currently the longest of any quantum memory system. A notable result is that hour-long coherence is maintained even at higher temperatures around 6 K, demonstrating the robustness of such systems at accessible temperatures. However, optical coherence is by far not in the same range (millisecond to second), but is still sufficient to enable long storage of optical qubits [77]. Considering single-ion experiments, for instance single $^{171}\text{Yb}^{3+}$ ions coupled to a YVO_4 photonic crystal cavity, spin coherence times of about 30 ms at > 1 K have been demonstrated [80]. These $T_{2,s}$ times are longer than typical gate operation times. As a conclusion, REI qubits can undergo many operations before losing coherence. The next step would involve integration into scalable, robust, and compact devices while maintaining long coherence times.

4. Universal set of quantum gates: The implementation of a universal set of quantum gate operations is a central requirement of quantum computing. Quantum algorithms are executed as sequences of unitary transformations $U_1, U_2, U_3, \dots U_n$, each acting on up to three qubits at a time. A unitary transformation is usually composed of single- and two-qubit gate operations and therefore represents the evolution of a quantum state. To be considered universal, the gate set must allow for the construction of any desired unitary operation through a configuration of simpler operations. Each implemented quantum gate corresponds to a specific Hamiltonian H_n generating a unitary transformation $U_n = e^{iH_n t/\hbar}$ over a time period t . Ideally, the physical apparatus allows control over all required Hamiltonians at the exact times they need to be activated. In reality, experimental setups are only capable of controlling certain Hamiltonians, typically involving two-qubit interactions, some of which cannot be selectively deactivated or switched, but the unwanted effects of the fixed interaction can be canceled by particular refocusing sequences of controllable interactions [3]. The most common two-qubit gate is the *Controlled-NOT* (CNOT) gate:

$$\text{CNOT} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad (2.4.1)$$

which applies a Pauli operation on the target qubit if the control qubit has the correct input state. In many systems, the CNOT gate is not directly available and must be synthesized from intrinsic interactions involving exchange or XY interactions between neighboring spins in combination with one-qubit operations. In conclusion, each implementation proposal must demonstrate how to achieve CNOT gates using the interactions that are naturally available. So far, the time profile of the two-qubit interaction pulse consists of a simple square shape, but in many cases more sophisticated pulse structures are required. Most qubits have a complex energy level structure, so that the applied Hamiltonian can cause couplings or transitions to higher energy states, resulting in leakage errors. In order to maintain the quantum system within the desired subspace, approaches with adiabatic processes can create smooth and slow transitions, as long as

the pulse duration fulfills the balance between adiabatic conditions and decoherence. One last point to mention is the classicality of the control apparatus. The interaction Hamiltonian is typically controlled by classical means such as laser intensity, gate voltages, or currents introduced via external control units. However, these devices are themselves composed of quantum mechanical parts. For effective operation, their action must remain classical, meaning that no entanglement should develop between any control devices and the quantum system. It is stated that this effect is negligible, but careful assessment is required for each specific case [3].

Another major challenge is the implementation of error correction, which requires multiple gate operations to be performed in parallel. Quantum systems relying on the so-called "*bus qubit*" to mediate the desired interaction may face additional limitations. Furthermore, gate operations have imperfections that introduce systematic and random errors. Both can be considered as decoherence processes. The tolerable error rate for random errors should be in the vicinity of 10^{-4} to 10^{-5} per gate operation, while systematic errors are harder to quantify. They must either be virtually minimized through careful calibration, or their presence can be detected and accounted for on the fly.

Status quo of criteria 4: Single-gate operations are possible and have been shown for both ensemble-based and single-ion REI qubits, as they can be driven coherently using strong optical pulses, microwave (MW) or RF control. Rabi oscillations or different echo-based sequences have been measured in systems containing Pr^{3+} , Eu^{3+} , Yb^{3+} , and Er^{3+} ions. Two-qubit gates are still under active investigation. Within the SQUARE project, magnetic or electric dipole blockade mechanisms are proposed to control the coupling between individual nearby single ions. For this purpose, two-color *secant hyperbolicus* (SECHYP) pulses were simulated and tested in single-qubit operation, with promising robust performance. So far, a high-fidelity two-qubit CNOT gate in an REI-based system has not been fully realized. First experiments have shown a two-qubit gate operation by using the electron spin of a single Ce^{3+} ion to detect a neighboring nuclear spin. As soon as CNOT operations can be reliably performed, a basis set of gate operations that is capable of performing any quantum gate is established, which requires near unity fidelities for practical quantum computation applications [33, 81].

5. Qubit-specific measurement capability: The final requirement for quantum computation is the ability to accurately measure the state of individual qubits. An ideal measurement delivers the outcome "*0*" with probability p and "*1*" with probability $1 - p$, independent of any other parameters and without disturbing the state of the rest of the quantum computer. In this case, the density matrix of a qubit is represented as $\rho = p |0\rangle \langle 0| + (1 - p) |1\rangle \langle 1| + \alpha |0\rangle \langle 1| + \alpha^* |1\rangle \langle 0|$, which contains all important parameters. If the performed measurement leaves the state of the qubit unchanged in addition to the reported outcome, the measurement is called "*non-demolition*" and can be used for state preparation, fulfilling already the second DiVincenzo criterion.

The quantum efficiency of an ideal measurement is 100 %, in reality, the efficiency is usually much lower, limited by factors such as noise, imperfect readout schemes, or other loss mechanisms. It is a useful measure to describe the success rate of detecting a signal. However, it does not provide any information about how accurately the detected signal matches the intended qubit state. The latter is called the *fidelity* of a quantum measurement. Both metrics are needed to conduct a complete analysis of the measurement process, but they do not necessarily have to correlate with each other. Although ideal values for quantum efficiencies are desirable, much less is sufficient to achieve reliable quantum computation. Valuable techniques to manage the tradeoff include, for example, redundancy created through the "*copy*" of the single output of one qubit to other additional qubits or *ensemble averaging*, where macroscopic numbers of qubits are excited simultaneously and the final measurement is performed as an ensemble average over the whole sample [3, 82, 83]. With respect to error correction, fast measurements on the timescale of 10^{-4} of the decoherence time are preferred, but not essential. If fast readout is not available, QEC is still feasible, as it requires more quantum gates to be implemented. In recent measurement schemes, it has been shown that if qubits can be initialized into maximally entangled pairs (*Bell states*) and two-qubit measurements in the so-called Bell basis ($\Psi^\pm = |01\rangle \pm |10\rangle$, $\Phi^\pm = |00\rangle \pm |11\rangle$) can be performed, then theoretically only one-qubit gates are sufficient for manipulation or measurement, but practically entanglement preparation as well as Bell basis measurements usually involve using two-qubit gates [3].

Status quo of criteria 5: The readout is usually performed with optical pulses. REI ensembles can be read out via the detection of echo signals or fluorescence. In photon echo AFC experiments using Pr^{3+} or Eu^{3+} ions, the coherent emission represents a collective effect and thus a qubit state, which is an averaged result and may differ from the response of single-ion detection. In general, individual qubits can be measured, however, the signal rates are relatively small, so that additional enhancement via cavity-mediated effects is required. Harnessing Purcell-enhanced emission in cavities has enabled significant progress in reading out the hyperfine state of a single Yb^{3+} ion with a fidelity of > 0.95 [80]. Similarly, the group of **Professor Jeff Thompson** demonstrated high-fidelity, single-shot readout (up to 0.88) of six individual Er^{3+} ions within a nanophotonic crystal cavity using optical frequency-domain multiplexing [84]. The SQUARE project also achieved optical detection and coherent control of single Ce^{3+} spins [33].

While the aforementioned criteria are sufficient for quantum computation, many practical QIP tasks such as secure communication (quantum key distribution) and distributed quantum computing also require the reliable transmission of quantum information. In order to account for these additional applications, two further requirements related to quantum communication must be fulfilled.

6. The ability to interconvert stationary and flying qubits and

7. The ability to faithfully transmit flying qubits between specified locations.

Although both criteria are closely related, they must still be considered separately, as certain tasks require only one of them to be met. The realization of *flying qubits* is typically achieved using photons, with the qubit encoded either in their polarization or spatial wavefunction, allowing efficient transmission through existing optical fiber networks. Coherent interconversion between stationary (e.g., spin) and flying photonic qubits has already been demonstrated [78, 85, 86] in several systems, but achieving efficient, scalable, and robust interfaces remains a central experimental challenge for many quantum emitter platforms and is essential for building large-scale quantum networks [3].

Status quo of criteria 6: Spin-photon interfaces have been demonstrated via quantum storage experiments. For instance, in $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$ and $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ optical storage has been shown by applying an AFC spin-wave protocol. Reported storage times are on the order of ≈ 500 ms for Eu^{3+} -doped crystals. Quantum memories with long storage times are key elements for long-distance quantum networks [76]. Another notable achievement was realized with single Er^{3+} ions implanted in CaWO_4 and coupled to nanophotonic cavities, where the coherent emission of indistinguishable photons at telecom wavelengths was demonstrated, representing a crucial step toward low-loss quantum communication over existing fiber networks [87]. In order to build a telecom-band quantum repeater based on single Er^{3+} ions, the implementation of an efficient and coherent spin-photon interface remains essential. Another demonstration of this criterion is the already mentioned entanglement and quantum state teleportation between two spatially separated $^{171}\text{Yb}^{3+}$ ions, each embedded in a remote YVO_4 nanophotonic crystal cavity. In this system, heralded photon detection was employed to create entanglement between the two solid-state spin qubits [78].

Status quo of criteria 7: The flying qubits of choice in REI-based systems are photons emitted at telecom wavelengths. As previously mentioned, single Er^{3+} ions offer promising characteristics for quantum communication applications. In ensemble-based protocols such as AFC, the emission, storage, and retrieval of photons have been successfully demonstrated. However, efficient coupling into fibers or integrated photonic devices remains under active development and investigation. In addition, heralded entanglement between two spatially separated $\text{Nd}^{3+}:\text{Y}_2\text{SiO}_5$ crystals has been achieved via the interference of a single photon on a 50:50 beam splitter, enabling the creation of a collective spin excitation delocalized between both nodes [88]. The demonstration of two remote $^{171}\text{Yb}^{3+}$ ions in YVO_4 nanophotonic cavities also satisfies this criterion, highlighting the scalability of such systems toward multi-qubit networks [78]. Together, these advances bring REI-based platforms closer to fulfilling the key requirements for long-distance quantum communication and distributed quantum computing.

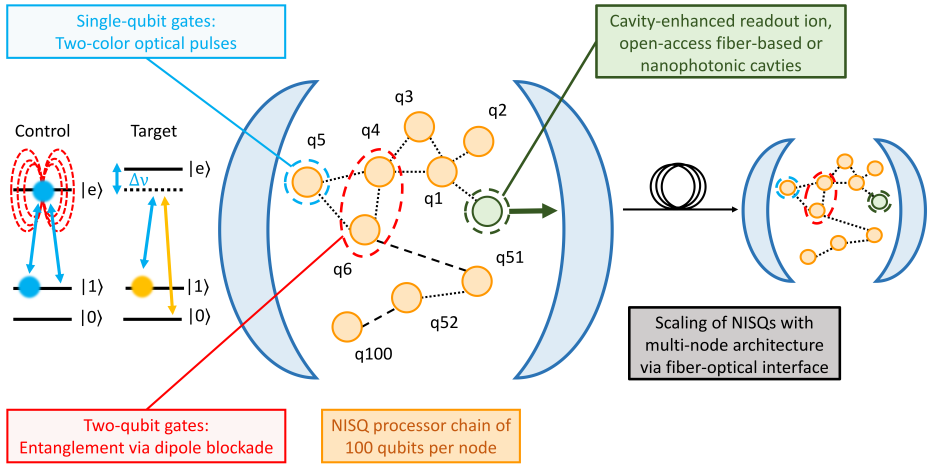


Figure 2.6: Concept of an REI-based scalable quantum computer. The schematic represents the main components required to realize an REI-based quantum computer, including the host material system, readout schemes, optical gate operations, a single processing node, and interconnectivity capabilities. Cavity-mediated readout can be implemented using fiber-based microcavities to enhance emission rates and detection efficiency. Gate operations are performed by applying tailored optical two-color pulses, while qubit–qubit interactions within a node are achieved by electric or magnetic dipole–dipole interactions (dipole blockade mechanism). Multiple processing nodes can be interconnected via optical fibers to form a scalable quantum network. The figure is adapted from [33].

2.4.2. Proposed concept of REI-based quantum architecture

As outlined in the criteria, recent experimental progress on REI-based material systems provides a unique combination of characteristics, including long spin coherence times, narrow optical transitions, and telecom-band compatibility, to realize essential quantum building blocks for scalable quantum technologies. This section presents a conceptual framework for a quantum computer based on REIs, as proposed in the SQUARE project roadmap by Adam Kinosh *et al.* [33], emphasizing the central components required for its realization. Given the variety of options available for each element, only the most relevant aspects are summarized here, with further details provided in the full SQUARE roadmap.

Building on the favorable properties of REIs, the SQUARE project proposes a scalable quantum computer architecture based on single REIs embedded in solid-state hosts. In this design, different REI species are assigned to specialized tasks: long-lived spin qubit ions (e.g., Eu^{3+}) serve as a quantum memory, while co-doped readout ions (e.g., Nd^{3+} or Er^{3+}), preferably emitting at telecom wavelengths, are Purcell-enhanced through microcavities for fast and high-fidelity qubit state detection. Entanglement and coherent

control within a node are achieved via the dipole blockade mechanism, enabling both single- and two-qubit gate operations realized by optical transitions. Figure 2.6 illustrates a schematic representation of a solid-state quantum processing node based on REIs, which can be scaled by interconnecting multiple nodes via optical fiber links.

The most promising host material for implementing this scheme is Y_2SiO_5 , doped with Eu^{3+} ions at a few percent level for qubit storage, and with trace amounts of another REI species at concentrations < 1 ppm as readout ions. The geometry of the host crystals also plays a crucial role, as it directly affects cavity integration and optical performance. Thin films or polished bulk crystals have proven to be promising candidates, as they preserve the desirable properties while enabling compatibility with different cavity designs. To reach readout fidelities exceeding 99 %, cavity-enhanced emission rates (high quality factors and low mode volumes of the cavity) of up to 10^7 photons per second must be established. In addition, these cycling processes can be further accelerated by selecting readout ions without nuclear spin, thus minimizing potential transition channels. Promising devices include open-access fiber-based microcavities [89] or scalable on-chip nanophotonic crystal cavities [78, 87]. The integration of superconducting detectors in on-chip devices would further increase the detection efficiency.

Single-qubit gates are performed by frequency-selective addressing via an optically excited state. To prevent high losses due to crosstalk, the gate bandwidth must be below 10 MHz, allowing local single-qubit operations with fidelity errors on the order of 10^{-4} . Two-qubit gates (entanglement) harness either magnetic or electric dipole–dipole interactions (dipole blockade mechanism) and can be performed with fidelity errors of $\sim 10^{-3}$. This error is higher than for single-qubit operations, since each two-qubit gate is composed of several single-ion operations, each of which introduces additional noise. The gate fidelities and the qubit connectivity can be improved via optimized protocols or cavity-mediated interactions, enabling new entangling mechanisms or long-range interactions between qubits.

A single REI-based node could host 50-100 individually addressable qubits using the available inhomogeneous broadening (~ 100 GHz) and doping concentrations of a few %, with connectivity introduced by the dipole blockade. Such a node would operate in the *Noisy Intermediate-Scale Quantum (NISQ)* regime, where a moderate number of qubits are available for quantum operations without the need for full quantum error correction [90]. Within a NISQ node, qubits can be uniquely addressed at high speed, entangled, and manipulated with the mentioned fidelities, enabling quantum computational tasks even in the presence of noise. The average connectivity per qubit will be about 10, with some ions exhibiting higher or lower connectivity. Finally, multiple NISQ qubit nodes can be interconnected via entangled photons emitted by the respective readout ions of each stationary node and heralded through interference at 50:50 beam splitters. This scaling approach is conceptually similar to strategies pursued with other material platforms, such as trapped ions or defect centers in diamond. REIs embedded in nanophotonic devices offer a particularly promising direction toward scalability, as miniaturization enables higher addressable qubit densities and improved photon collection efficiencies.

Furthermore, recent advances with Er^{3+} ions have demonstrated the generation of indistinguishable photons at telecom wavelengths, which is especially advantageous for low-loss transmission in fiber-based long-distance connections [87].

In conclusion, the combination of exceptional optical and spin properties, telecom wavelength compatibility, cavity-enhanced photon generation, and the potential for on-chip integration positions REIs as a highly promising platform for building scalable quantum processing nodes, enabling future quantum technologies [33].

3. Experimental setup

In this chapter, we provide a detailed overview of the experimental infrastructure employed to investigate the intrinsic physical properties of Eu^{3+} -based molecular complexes. The initial setup was built by **Christina Ioannou** during her master's thesis [57]. Since then, it has been incrementally modified and complemented with new hardware and software, also accompanied by collaboration on subsequent master's theses by **Weizhe Li** and **Vishnu Unni C.** [45, 62]. The central components include a high-power and narrowband laser system, the excitation and detection paths, the control and data acquisition (DAQ) unit, the sample holder and its implementation into the cryogenic environment. As there was no dedicated low-temperature cryostat for the ensemble spectroscopy, a self-made dipstick exchange gas cryostat was built and used during most spectroscopic measurements. In order to analyze several samples in one experimental run, this cryogenic setup was modified in the early stages and later replaced by newly developed so-called *flange dipsticks*. At a later stage, measurements were performed using a dilution refrigerator, enabling measurements at millikelvin temperatures to improve optical properties and reduce thermal decoherence effects. To facilitate these low-temperature measurements, a custom-designed, fiber-based sample holder was used. During the initial implementation of ensemble spectroscopy experiments in our lab, a crucial bottleneck was the integration of samples into the cryostats. This challenge arose primarily from the powder-like structure of the sample, which complicated thermal anchoring and the achievement of an optimal configuration for both efficient excitation and reliable signal collection under cryogenic conditions. The initial concept and design of the sample holder were introduced by **Xiaoyu Cheng** [91], which was later adapted and modified to ensure compatibility with various cryogenic systems and sample geometries used throughout this work. In the following, each experimental component is summarized and presented according to the current state of the art. The most recent hardware modification was the implementation of a cylindrical coil for full RF control, enabling the investigation of the spin properties of the REI-based molecular complexes. As a brief remark, the experimental description of our cavity setup is provided in Chapter 5. This separation was intentional, as cavity-based spectroscopy relies on different experimental methods and configurations.

3.1. Laser system

The laser system integrated into our experimental setup is based on the *Sirah Matisse-2-DX dye laser*, a ring dye laser stabilized via the Pound–Drever–Hall (PDH) technique. The central requirements in coherent ensemble spectroscopy are stable laser operation with small or negligible frequency shifts over the timescale of a single measurement (microsecond to second timescales), a narrow laser linewidth and the capability to tune the laser frequency over wide spectral ranges. Although the dye laser concept is gradually becoming outdated and more advanced systems are available on the market, it still remains a robust and reliable system requiring minimal maintenance. According to the specifications provided by the manufacturer [92], this laser system fulfills our demands for high-resolution spectroscopy with REIs, as it provides excellent frequency stability as well as a narrow linewidth (< 100 kHz root mean square (RMS)) relative to its internal reference cavity and allows continuous frequency tuning over a broad range exceeding 60 GHz. The reference cavity unit is responsible for both stabilizing the narrow laser linewidth and acting as the frequency reference when the laser is scanned across different frequencies. These capabilities enable precise addressing of narrow optical homogeneous linewidths.

To maintain clarity and focus, only the key components are mentioned and discussed. This section describes the general configuration of the laser system, while the optical elements needed to determine and tune the emission frequency are additionally listed in Subsection 3.1.1. The working principle of the PDH frequency stabilization is outlined in Subsection 3.1.2. Figure 3.1 illustrates the optical layout of the laser system, including the dye laser head at the bottom and the reference cavity unit at the top. Our laser system is based on a dye configuration using *Rhodamine 6G* (R-6G) dissolved in ethylene glycol at a concentration of 0.75 g L^{-1} as the gain medium, covering a typical spectral bandwidth from approximately 560 nm to 620 nm. This wavelength range allows for the study of different REI species, including not only Eu^{3+} , but also Pr^{3+} , for example, which emit at about 579 nm to 581 nm (in most host materials) and 606 nm to 608 nm (in Y_2SiO_5), respectively. The dye solution is circulated within a closed-loop compressor unit, producing a dye jet in free space through a nozzle within the laser system. The dye is pumped by a *Spectra-Physics Millennia eV* laser, delivering up to 15 W of output power, which is coupled via a free-space port into the main laser segment and deflected by a focusing mirror onto the dye jet. The distance between the focusing mirror and the dye jet determines the lasing threshold. As a quick side note, utilizing the maximum output power leads to rapid bleaching of the dye, such that dye exchanges are required every 4 to 6 months. The resulting laser beam, emerging due to stimulated emission, is then guided by two folding mirrors into the ring resonator, following the paths in both the clockwise and counter-clockwise direction. Besides the focusing mirror, the folding mirrors, or more specifically the distances with respect to each other and to the dye jet, can be considered as critical parameters, as their non-optimal alignment can lead to deviating mode shapes, fluctuating output power, multi-mode operation or *beam flickering*. This latter behavior is characterized by abrupt jumps between lasing and

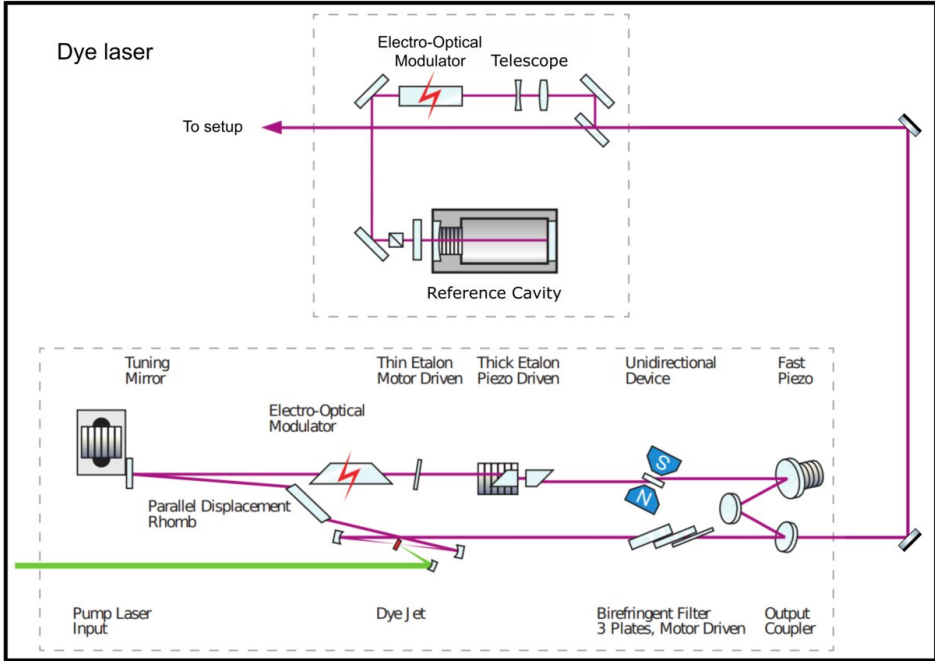


Figure 3.1: Optical layout of the Sirah Matisse 2DX Dye laser. The pump laser beam, here denoted as the green path, excites the dye jet, which in this case consists of R-6G dissolved in ethylene glycol. The dye operates as the gain medium, resulting in fluorescence centered around 580 nm. The emitted light, here represented as the purple path, is amplified within the ring resonator, passing through various frequency-selective elements and is finally guided toward the reference cavity unit via an output coupler. Due to the specific functionalities and arrangement of the optical elements, both the frequency output range of the laser and the unidirectional outcoupling of propagating modes can be precisely controlled. The reference cavity is required to enable frequency stabilization schemes. Upon successful operation, the laser system provides single-mode and frequency-stabilized output. The schematic diagram is adapted from the Sirah device manual [92].

non-lasing operation. Nevertheless, in the case of a well-aligned ring resonator, the dye laser beam can be amplified and can deliver output powers of up to 2.2 W. As depicted in Figure 3.1, the amplified laser beam partially leaves the main laser segment through an output coupler, while the remaining fraction is reflected back into the ring cavity. Finally, the beam is directed into the reference cavity unit. Within this segment, the laser beam is split again: one path guides the laser beam to the reference cell, while the other path forms the output of the entire laser system. In order to achieve single-mode and frequency-stabilized laser operation, the system relies on specific optical elements as well as the PDH locking technique, which will be discussed in the following [92].

3.1.1. Frequency-selective elements

As optical resonators have discrete resonances with defined resonance frequencies, one central parameter is the free spectral range (FSR), which is given by the separation between two adjacent resonances. Mathematically, the FSR is described as $\Delta\nu = c/d$, where c is the speed of light, and d denotes the cavity mirror distance of the whole ring resonator. The FSR of our *Matisse-2-DX* model is about 160 MHz. In combination with the particular configuration of the birefringent and polarization-selective optical elements, the mode spectrum of the laser, and thus the FSR, can be adjusted, enabling broad frequency selection. The following components are essential to establish and control single-mode operation of the dye laser [92]:

1. **Birefringent filter:** The birefringent filter (BiFi) is composed of three rotatable plates, which can be controlled via a stepper motor. This element serves as a coarse bandpass filter that determines the approximate output wavelength of the ring resonator. Tuning the laser wavelength is accomplished by rotating the filter. The frequency range of available modes is narrowed down to 50 GHz, which corresponds to an FSR of the BiFi of about 130 nm.
2. **Fabry–Pérot etalons:** An optical etalon acts as a solid-state Fabry–Pérot resonator, serving as another adjustable frequency filter. There are different geometries or configurations to realize an etalon, provided that it possesses two dedicated parallel reflecting surfaces. To fulfill the conditions for constructive interference, many mechanisms can be implemented, including frequency modulation and variation of the etalon spacing or the angle of incidence. In the case of the dye laser, two Fabry–Pérot etalons are built-in to further tune the output frequency and in addition, to achieve single-mode as well as single-frequency operation. The first etalon, referred to as the *thin etalon*, is a thin glass plate, which is controlled by a stepper motor to vary the angle of incidence, thereby serving as a coarse bandpass filter featuring an FSR of 250 GHz. The thin etalon is immediately followed by the second, the *thick etalon*, consisting of two prisms with parallel base sides and an air gap in between. One of the prisms is attached to a piezo actuator to actively modulate the air gap thickness. The resulting FSR of this etalon is on the order of 20 GHz. Since the spacing is controlled by an active feedback loop, only one longitudinal laser mode is selected within the filtered spectral window.
3. **Piezo-mounted mirrors:** Two mirrors within the configuration are mounted on piezoelectric actuators. According to Figure 3.1, one mirror is located at the top-left corner of the dye laser head, referred to as the *tuning mirror* or *slow piezo mirror*, while the second is positioned at the top-right corner and represents the *fast piezo mirror*. When both piezos are modulated, the optical path length of the ring resonator can be dynamically adjusted. These mirrors are primarily required for the feedback loop of the PDH frequency stabilization scheme. While the fast piezo mirror reacts to fast perturbations to reduce the

effective laser bandwidth, the slow piezo mirror scans the laser to a resonance of the reference cavity and thus compensates for slow frequency drifts.

4. **Electro-optic modulator:** The electro-optic modulator (EOM) can be used for high-speed frequency modulation or high-bandwidth corrections in feedback control loops, such as in the PDH locking technique. Our laser system incorporates two EOMs, one located in the main laser segment and the other positioned in the reference cavity unit.
5. **Unidirectional device:** In order to prevent two counter-propagating modes with the same frequency in the ring laser, an optical diode setup is implemented, consisting of a so-called *Faraday rotator* and an *out-of-plane mirror*. Both components are capable of rotating the polarization. In this configuration, the Faraday rotator includes a Terbium–gallium–garnet crystal plate placed within a strong magnetic field, causing a rotation of the polarization vector that is independent of the propagation direction. The out-of-plane mirror is located between the fast piezo mirror and the out-coupler, but it is mounted at a different height compared to the other optical elements. In this case, the rotation of the polarization becomes direction-dependent, leading to either a cancellation of the polarization effects for the counter-clockwise guided mode or a series of detrimental optical losses in the resonator for the clockwise guided mode. As a result, only one propagation direction is favored, effectively establishing unidirectional operation.

In conclusion, the final single-frequency output mode arises from both the configuration and the sequential filtering effects of the controlled or motorized optical components, especially the birefringent filter as well as the thin and thick etalons. In the next section, the technical requirements for implementing active frequency stabilization of the laser system are summarized.

3.1.2. Laser stabilization

To avoid frequency fluctuations and drifts over time, the laser system is equipped with a reference cavity unit, which employs the PDH frequency stabilization technique. The reference cell constitutes the central element of this configuration, serving primarily as an external frequency reference, for which the resonance frequency must remain very stable over time. For this reason, the reference cell utilizes a highly robust and scannable Fabry–Pérot cavity design, along with materials of low thermal expansion, including macroscopic mirrors in a non-confocal arrangement mounted in an *INVAR*³ rod. In addition, the whole resonator is evacuated to further improve the thermal stability and minimize acoustic noise [57, 92].

³ Nickel–iron alloy

3. Experimental setup

Within the reference cavity unit, the laser beam is divided by a beam splitter, so that a fraction of the laser beam is directed toward the reference resonator and can be used as an input signal for feedback loops to counteract possible fluctuations. Along this optical path, a telescope setup based on two lenses is installed with the purpose of mode-matching the laser beam from the main laser segment to the fundamental mode of the reference cavity. This is followed by an EOM, acting as a phase modulator. If the EOM is modulated sinusoidally with a frequency ν_{mod} , the frequency spectrum of the initial laser frequency ν_0 will be modified after leaving the EOM, where it exhibits sidebands at $\nu_0 \pm \nu_{\text{mod}}$ around the carrier frequency ν_0 . If the reference cavity is resonant with the fundamental laser frequency ν_0 and possesses a sufficiently high finesse, only this component of the laser beam can couple into the reference cavity. As a consequence, the sidebands $\nu_0 \pm \nu_{\text{mod}}$ are not covered by the linewidth of the resonator and are reflected back by the first mirror of the reference cavity. Additionally, the excited light field within the reference cavity can also be out coupled via both cavity mirrors, which is required to observe the reflected and transmitted reference cavity signals. The reflected sidebands and the out coupled cavity light field are directed via a beam splitter to a *fast photodiode*. Due to the modulation of the EOM, the detected signal is composed of not only a constant component but also multiple beat frequencies, arising from various interference processes between carrier and sidebands. The simplest form of the occurring beat frequencies is given by the EOM modulation frequency ν_{mod} , which can be used to generate a suitable frequency error signal by mixing it with the diode signal. In general, the mixing process involves many additional steps, but for the sake of clarity these are omitted here and detailed descriptions or schematic layouts are provided in the documentation from *Sirah* [92].

Figure 3.2 illustrates the resulting PDH error signal after the mixing process. The parameters used to generate this plot were taken from the manual [92]: the *FSR of the reference cavity* is 1320 MHz, the *finesse* is 250, and the *EOM modulation frequency* is 20 MHz. The line shape of the PDH signal corresponds to the derivative of the reflection signal, which is antisymmetric and features a steep slope at zero frequency detuning. The PDH stabilization scheme is a highly sensitive technique for detecting the laser frequency detuning relative to the resonance of the reference cavity, which corresponds to an optical phase shift of the reflected signal and thus a non-zero PDH error signal. Due to its characteristic steep slope at zero detuning, the PDH error signal enables the implementation of a precise feedback loop to correct even extremely small frequency shifts, which in turn can be used to lock the laser frequency to the reference cavity. An important point to emphasize here is that the PDH technique detects phase shifts rather than frequency shifts or intensity fluctuations, making it insensitive to laser intensity noise. The capture range for corrections is determined by the EOM modulation frequency ν_{mod} , as the PDH error signal is exactly zero again at this detuning, which can be seen in Figure 3.2. Up to this point, we have discussed the *static* case, where the laser frequency is stabilized at a fixed frequency value. However, if a broader frequency range needs to be scanned, the reference cavity itself can be used for this purpose. Since the reference cavity is scannable, its cavity length can be varied to shift the resonance condition. The laser, being phase-locked to the reference cavity via the PDH stabilization

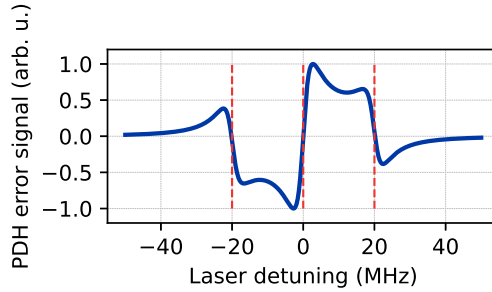


Figure 3.2: Theoretical PDH error signal of the reference cavity. The graph shows the theoretical behavior of the PDH error signal as a function of laser detuning. The parameters used for plotting were taken from the device manual [92]. Given a finesse of $\mathcal{F} = 250$ and a free spectral range of $\nu_{FSR} = 1320$ MHz, the cavity linewidth can be calculated by applying the formula $\mathcal{F} = \nu_{FSR}/\Delta\nu_0$. Together with a modulation frequency of $\nu_{mod} = 20$ MHz, which generates the two sidebands (dashed red vertical lines) around the cavity resonance (equal to the carrier frequency) $\nu_0 \pm \nu_{mod}$, the PDH error signal (solid blue line) can be derived accordingly. The signal exhibits a dispersive (*S-shaped*) profile centered around zero laser detuning, with a steep linear slope (indicated by the dashed red vertical line) near the resonance, making it ideal for locking schemes and thus frequency stabilization.

scheme, will automatically follow this change. This enables high-resolution frequency scans while maintaining an actively stabilized operation mode.

Our laser system utilizes multiple feedback loops in order to stabilize the laser frequency. Within the main laser segment, an additional EOM with a larger control bandwidth is installed, which is connected to the main PDH unit, to complement the feedback processes and to further improve the laser bandwidth as well as stability. Additional optimization can be achieved by employing a more stable, custom-built reference cavity combined with suitable PDH electronics. Although the laser system is very reliable during measurements, the piezo-driven optical elements can introduce frequency drifts due to slow discharge or piezo creep effects. Nevertheless, the laser can remain locked and ensure stable operation for several hours.

3.2. Optical setup and experimental control

A frequency-stabilized laser system with single-mode operation is the basis of each ensemble spectroscopy setup. However, the high-power output laser beam requires additional treatment and control mechanisms to be used in advanced spectroscopic measurements with high resolution. Several optical elements and signal-generating devices are included in the main setup in order to enable continuous-wave operation or pulse shaping by frequency and amplitude modulation. Figure 3.3 illustrates the optical

3. Experimental setup

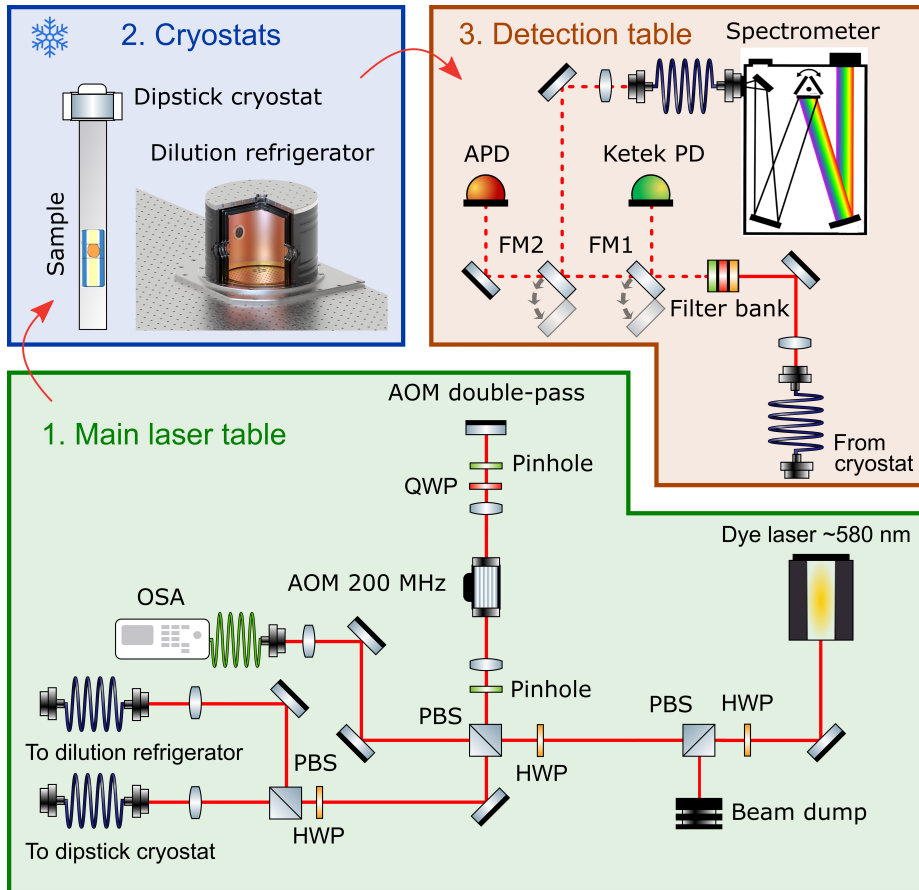


Figure 3.3: Optical setup for ensemble spectroscopy. The overall setup is divided into three main parts: laser beam preparation (green box), coupling into cryostats (blue box), and detection of the transmitted signal through the sample (brown box). In order to enable frequency and amplitude modulation, the laser light is guided through the acousto-optic modulator operating in a double-pass configuration. Additionally, the output frequency of the laser is monitored by an optical spectrum analyzer to monitor possible frequency shifts or jumps. Once the required modulation is adjusted, the light can be fiber-coupled into different cryostats, including our home-built dipstick cryostats or commercially available dilution refrigerators. The incorporated sample holder is fully fiber-based, so that the transmitted signal through the sample can be easily directed to the detection path, where it can be filtered and thus analyzed either via avalanche photodiodes or a spectrometer. The modulated and collected light is represented as solid lines, while the filtered light is represented as dashed lines. The red color does not imply the wavelength of the collected signal and was chosen for clarity. The schematic layout was created with Inkscape and the Component Library [93].

setup and the corresponding hardware devices installed for experimental control. In this section, the optical paths comprising excitation and detection, and the experimental control unit, are presented. The latter involves the hardware for signal generation and data acquisition, realized via a *Python*-based graphical user interface (GUI). All described elements of the optical setup are sufficient to perform a set of ensemble spectroscopy measurements required to fully characterize a new sample in the optical domain. For coherent spin control, the same hardware can be used, since only one additional output channel is needed to provide an RF signal to the cylindrical coil (see Subsection 3.3.1). In general, two output channels are required to conduct spin-related measurements: the first one controls the laser beam for both excitation as well as readout, and the second one is responsible for spin manipulation. For this reason, only basic pulse sequences were programmed and tested, complex schemes which would require simultaneous multi-channel signal generation ($> \text{two channels}$) are not considered here.

3.2.1. Excitation path

As depicted in Figure 3.3 (green box), the frequency-locked laser beam leaves the reference cavity unit toward a first polarizing beam splitter (PBS) cube in order to adjust the laser output power and thus direct a large fraction of the power onto a beam dump. The transmitted power through the PBS is usually adjusted to about 500 mW, constituting an upper limit for the damage threshold for several optical elements within the setup. Afterwards, the attenuated laser beam passes through a second PBS cube and can be either guided to a fiber coupler, which is connected to an optical spectrum analyzer (OSA)⁴ for monitoring the laser linewidth and frequency, or reflected to an acousto-optic modulator (AOM)⁵ assembled in a double-pass configuration. The spectral resolution of the OSA, which is defined as the measured FWHM intensity of an infinitely narrow optical signal, is specified to approximately 4 GHz, together with an optical rejection ratio of greater than 40 dB. The AOM path serves as a gating and pulse-shaping device for the laser beam. Depending on the parameters of the RF signal applied to the AOM, the transmitted light through the AOM can be simultaneously detuned in frequency and modulated in amplitude. A more detailed explanation of the working principle of the AOM in a double-pass configuration, and its implementation into both the hardware and software environment, is given in Subsection 3.2.3. After leaving the AOM path, the laser beam is finally directed onto a third PBS cube, which splits the modulated light into two fiber-coupling devices connected to single-mode fibers, which lead to two different cryostats (blue box) used throughout the experimental work presented in this thesis, which incorporate the sample under investigation. The upper branch is connected to the optical port of the dilution refrigerator, while the lower one can be attached to the optical feedthroughs of one of our home-built dipstick cryostats. Each PBS cube possesses a half-wave plate (HWP) in front of it, so that the combination of

⁴ Model: 771 *Spectrum Analyzer*, purchased from *Bristol Instruments*.

⁵ Model: AOMO 3200-121, purchased from *Gooch & Housego*.

both optical elements allows adjustment of the laser output power of the individual optical paths according to the required parameters of the corresponding measurements. Due to this possibility, different measurement methods and power regimes are available and can be utilized to explore more specific material properties [57, 62].

3.2.2. Detection path

The fiber-coupling devices, as shown in Figure 3.3, guide the laser beam toward the sample integrated in the corresponding cryostat. Since the sample holder is a fully fiber-based component, the transmitted light through the sample, or emitted fluorescence, can be easily directed into our stationary detection path (brown box), which is identical for all examined samples. The optical layout of the detection path is shown in the upper right corner of Figure 3.3. The collected light from the sample is outcoupled and collimated via a fiber-coupling device. Afterwards, the signal can be either filtered by a longpass filter ⁶ to remove the excitation light and thus detect the fluorescent response of the sample, or by a bandpass filter ⁷, centered around 580 nm, to pass through the transmitted absorption signal. Additional filters can be added to the filter bank to further narrow down spectral bands for detection or to attenuate strong transmission signals, thereby preventing saturation of the detectors. In a final step, the collimated and filtered signal can be either focused onto a photodetector or fiber-coupled into a commercial spectrometer ⁸, which allows for the recording of photoluminescence spectra through the use of a flip mirror. Depending on the required bandwidth or sensitivity of the detecting device, a second flip mirror can be used to direct the light onto a very sensitive photodetector ⁹, which is useful for measurements approaching the noise level. In the absence of the flip mirror, the collected signal is focused onto an avalanche photodiode (APD) ¹⁰, which features a higher bandwidth than the KETEK photodetector and is advantageous for detecting frequency-detuned beat signals [57, 62].

For the ensemble spectroscopy measurements performed on samples integrated into the dilution refrigerator, the same excitation and detection paths can be utilized, since the incorporated sample holder is modified but still fully fiber-based. In this case, the sample geometry, especially for macroscopic and bulky crystals, only allows excitation via one of the free-space optical windows of the dilution cryostat. The modulated and fiber-coupled light needs to be outcoupled and collimated again before being directed toward the sample. The transmitted signal is reflected via a stationary mirror positioned inside the cryostat toward another free-space output window. The corresponding sample is attached to a copper mount, which thermalizes the sample to the temperature of the cold plate of the dilution refrigerator. The transmitted light through the cryostat is

⁶ Model: BLP01 594 R-25, purchased from Semrock.

⁷ Model: FB580-10, purchased from Thorlabs.

⁸ Model: Andor Shamrock-500i-D2-SIL-R, purchased from Oxford Instruments.

⁹ Model: KETEK PE3315-WBTIA-SP, purchased from KETEK.

¹⁰ Model: APD430A2, purchased from Thorlabs.

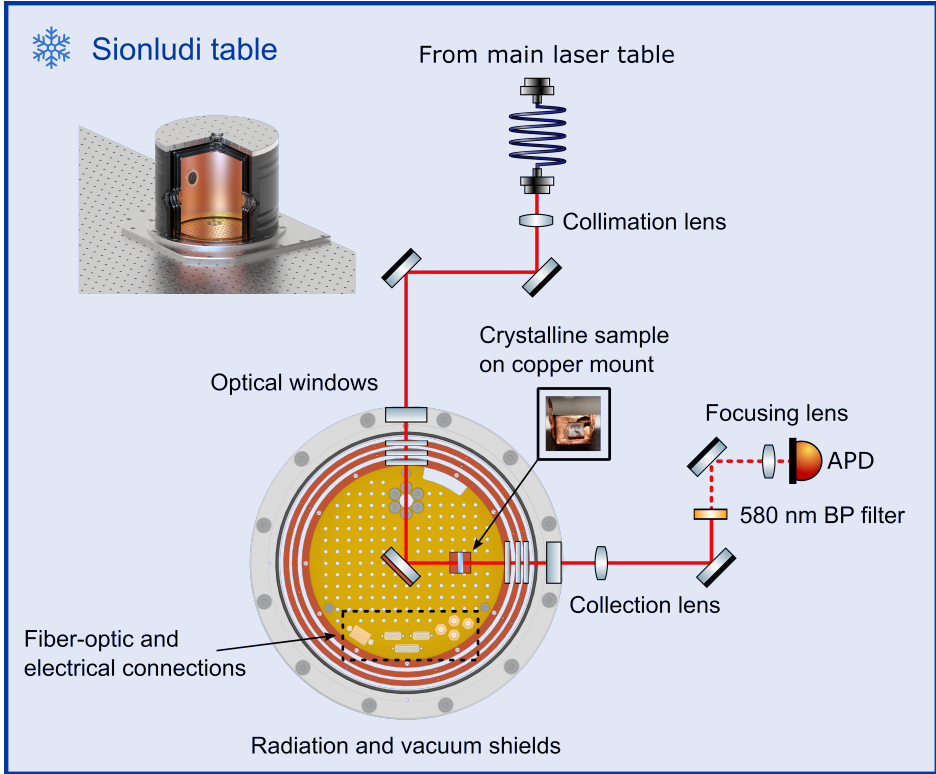


Figure 3.4: Optical setup for measurements of macroscopic samples. The modulated light is coupled to the cryostat table via a single-mode fiber. For the spectroscopy of macroscopic crystalline samples, free-space excitation and collection of the transmitted signal are required using the optical windows. To guide the light toward the sample, a mirror is attached to a custom-built mirror holder, whereas the sample is mounted on an additional post. Both holders are made of copper to support thermalization. The transmitted signal through the macroscopic crystal is then collimated by another lens, in order to increase the collection efficiency. Afterwards, the collected light is filtered and focused onto an APD. As in the case of the main optical schematic layout, the same style guide is applied here. The modulated and collected light is represented as solid lines, while the filtered light is represented as dashed lines. The schematic layout was created with Inkscape and the Component Library [93].

then filtered by a bandpass filter centered at 580 nm and focused onto the APD. The adapted optical layout for the free-space measurements of macroscopic samples within the dilution cryostat is illustrated in Figure 3.4. Due to spatial arrangement issues during the sample integration and the consequent non-optimal alignment of the optical components, an additional lens was installed outside the cryostat, directly after the output optical window, in order to correct for the diverging character of the outcoupled laser beam and, hence, to improve the collection efficiency [62].

3.2.3. Frequency and amplitude modulation

The central component of the experimental control unit in our optical setup is an arbitrary waveform generator (AWG), which provides various waveform types, including sine, square, and triangular waveforms, as well as multiple modulation modes, such as amplitude, frequency, phase, and in-phase and quadrature (IQ) modulation. Initially, an AWG from *Keysight Technologies*¹¹ was employed to generate the pulse sequences required for optical ensemble spectroscopy. However, since this device was shared with an optical cavity experiment focused on detecting single europium ions, the capabilities of the overall experimental setup were constrained, particularly when progressing toward coherent spin control, where the simultaneous application of multiple pulses is essential. To overcome these limitations, the Keysight AWG was replaced by a more advanced system from *Quantum Machines*¹², specifically designed for pulsed and complex measurement protocols aimed at coherent multi-qubit control. While both AWGs differ in hardware specifications, their operational principles and integration into the experimental architecture are largely analogous. Notably, both devices incorporate a field-programmable gate array (FPGA), which allows for fast internal real-time calculations, signal processing, low-latency feedback protocols, and precise timing, meeting the substantial requirements for complex and synchronized pulse protocols in advanced quantum experiments. Each device is equipped with both analog and digital output channels, enabling full control over parameters such as sampling rate and frequency detuning. Furthermore, they support synchronization with external instruments and provide transistor–transistor logic trigger signals for coordinated readout schemes and multi-channel operation. The DAQ can be configured either in a closed loop with the AWG, allowing for direct real-time signal processing, or alternatively via an oscilloscope, where the recorded data is post-processed. The latter is the most commonly used method in our experiments, as it is easier to implement, despite requiring longer acquisition times. In both cases, the signal typically detected by an APD serves as the input to the DAQ system. The following description outlines the control setup currently employed in our experiments, beginning with the AWG, followed by the double-pass configuration of the AOM, and concluding with the Python-based user interface.

Keysight and Quantum Machines AWG devices: The waveform and modulation capabilities of the Keysight AWG are based on an integrated FPGA architecture equipped with four independent analog output channels. Each channel features a built-in function generator capable of producing standard carrier signals with bandwidths of up to 200 MHz. As previously mentioned, various modulation types are supported, including simultaneous modulation in amplitude and frequency. The modulation relies on user-defined waveforms represented as numerical sequences ranging from -1 to $+1$ as a function of time. These sequences are then mapped to corresponding voltage

¹¹ Model: *M3300A*

¹² Model: *OPX+*

or frequency deviations depending on the selected modulation mode. Together with parameters such as carrier frequency and sampling rate, the precise shape and temporal evolution of the output signal can be fully determined. The maximum sampling rate of each output channel is specified at 500 MS s^{-1} , while the output voltage range typically spans from -1.5 V to 1.5 V [94].

The OPX+ device from Quantum Machines is specifically engineered to meet the technical demands of real-time control and precise synchronization essential in modern quantum experiments. At the heart of the OPX+ lies the *pulse processing unit (PPU)*, an FPGA-based core processing module that integrates multiple independent waveform generators, digitizers, and sub-processing units. These components are embedded in a scalable architecture and are interconnected via a high-speed communication back-plane, ensuring synchronized timing (referenced to an internal clock), efficient signal routing, and ultra-low latency response across the communicating modules. The RF front end of the OPX+ features high-performance Digital-to-analog converters (DACs) and Analog-to-digital converters (ADCs), specifically optimized for the integration and control of external devices such as AOMs, detectors, and MW or RF systems.

The combined system enables real-time execution of compiled pulse sequences with sub-microsecond latency. Unlike conventional AWGs that rely on predefined waveforms, the OPX+ utilizes a fully parameterized time-domain waveform generation, with real-time control over amplitude, frequency, phase, duration, measurement axes, etc. This is accomplished via the commercially provided *QUA (Quantum architecture)* programming language (see Python-based GUI), which supports dynamic signal generation, conditional logic, and adaptive feedback mechanisms. Designed pulse sequences are compiled and uploaded to the PPU, allowing the experiment to be executed autonomously without requiring real-time communication with an external computer. When the experiment is performed, the FPGA executes the precompiled pulse instructions, and the resulting control signals are generated through the DACs and ADCs before being routed to the appropriate output channels for interaction with external devices. Due to the ultra-low latency of the system, real-time measurements with conditional branching become possible. For instance, the pulse sequence can be interrupted, restarted, or dynamically modified based on detector input signals, thereby enabling high-speed feedback loops and flexible control schemes essential for quantum measurement and error correction protocols.

Depending on the acquired model, the OPX+ offers four to ten analog output channels, two analog input channels, and ten digital output channels. Each analog output channel supports a maximum sampling rate of 1 GS s^{-1} , an output bandwidth of up to 400 MHz ¹³, and an output voltage range from -0.5 V to 0.5 V . Additionally, all channels provide IQ modulation capabilities, allowing for the generation of arbitrary spectral profiles. Due to the lower output voltage compared to the Keysight AWG, an additional

¹³ Optional upgrade to the *QM Octave model* enables the generation of output signals with frequencies ranging from 2 GHz to 18 GHz .

3. Experimental setup

preamplifier¹⁴ is employed in front of the main amplifier to supply the necessary drive power for the AOM controller. The digital output resolution is approximately 1 ns, while a built-in internal 1 GHz clock ensures phase coherence and precise timing synchronization across all output channels, including across multiple OPX+ units when used in scalable configurations [95].

In conclusion, the OPX+ offers the performance and flexibility required for advanced multi-qubit control, real-time feedback, and error-corrected quantum algorithms, making it a highly capable alternative to the Keysight AWG.

AOM and double-pass configuration: An AOM is a versatile device commonly used to modulate the amplitude, frequency, or propagation direction of laser beams, operating on the principle of Bragg diffraction. Modulation arises from the deflection of the incident light by acoustic waves propagating within a crystalline medium, typically quartz, which induce a periodic variation in the refractive index and cause diffraction. The desired modulation signal is first generated by the AWG and subsequently amplified before being sent to the AOM controller. From there, the resulting RF signal is delivered to the AOM, where it is converted into an acoustic wave via a piezoelectric transducer. The overall AOM control chain is schematically illustrated in Figure 3.5.

Since the modulation frequency determines the deflection angle of the outgoing beam, even small changes can lead to beam misalignment, which is particularly problematic for single-mode fiber coupling. In order to compensate for this effect, the AOM is operated in a double-pass configuration, ensuring that the beam retraces its original path and preserves alignment after reflection. In this setup, the first-order diffracted beam is reflected back through the AOM by a mirror, causing it to interact with the acoustic waves twice and thus leading to double the frequency shift. As a result, angular deviations induced by modulation frequency changes are effectively canceled, significantly improving the beam pointing stability. To enable spatial separation of the modulated and non-modulated original beams, a quarter-wave plate (QWP) and a PBS cube are inserted into the optical path. On the first pass, the QWP introduces a 90° phase shift between the fast and slow axes of the polarization components, converting the linearly polarized light into circular polarization. After reflection and the second pass through the QWP, the light undergoes an additional 90° phase shift, resulting in a net 180° phase shift. This converts the light back into linear polarization, but rotated by 90° relative to that of the original incoming beam. This polarization rotation allows the PBS cube to separate the returning, modulated beam from the original path, thus enabling efficient spatial isolation of the frequency-shifted output [57, 96]. A schematic representation of the double-pass configuration used in our optical setup is provided in Figure 3.5.

¹⁴ Model: ZSW, purchased from *Mini-Circuits*.

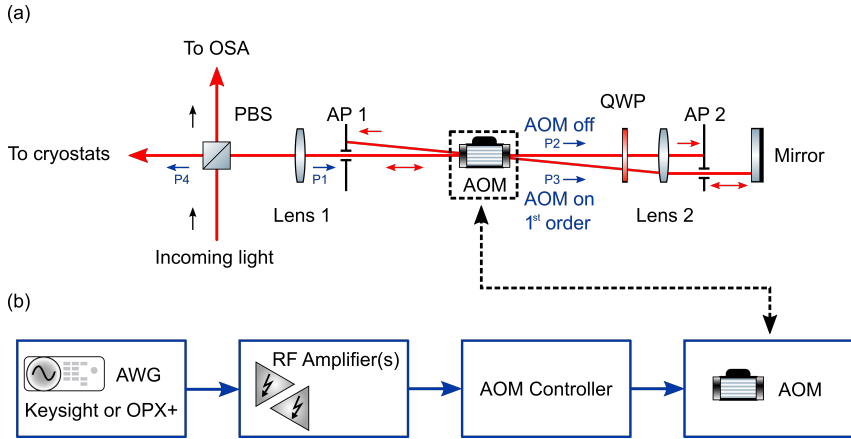


Figure 3.5: AOM double-pass configuration and control chain. (a) The beam path shown corresponds to one part of our experimental setup. The laser beam first encounters a PBS cube, where it can be directed either toward the OSA or the AOM. The reflected beam is focused onto the AOM by the first lens through an aperture (AP1). If the AOM is not driven, the beam passes straight through and is blocked by a second aperture (AP2). When the AOM is active, the first diffraction order can be collected and redirected back toward the AOM by a fixed mirror. All laser beams emerging from the AOM are collimated by a second lens. Both lenses are identical in focal length, with their focal points aligned at the center of the AOM. A QWP positioned in the beam path after the AOM is used to modify the polarization of the light, enabling the separation of beams at the PBS cube. Since both the QWP and AOM are passed twice, only the first-order diffracted beam is transmitted and directed back toward the PBS cube. As a result, the incoming and modulated beams can be separated due to their orthogonal polarizations. The blue vectors denote the laser beam power levels at the corresponding locations, primarily required to determine the diffraction and double-pass efficiencies of the AOM. The figure is adapted from [97]. (b) The schematic diagram shows the RF control path for driving and modulating the AOM. The signal generated by an AWG is amplified and then passed to the AOM driver. Depending on the AWG model, multiple amplifiers are required to deliver the correct output power. The driver actuates a piezoelectric transducer inside the AOM, which finally generates acoustic waves within the corresponding crystal. This enables the diffraction of the incoming laser light and, based on the RF input signal, modulation in amplitude and frequency can be achieved. The figure is adapted from [57]. Both schematic diagrams were created with Inkscape and the Component Library [93].

Python-based GUI: Communication with both AWGs is established via Python-based interfaces and the corresponding libraries provided by the manufacturers. In the case of the Keysight device, a custom GUI was developed by **Christina Ioannou** in order to enable user-friendly control over the complex functionalities of the AWG. The core components of this interface are based on the existing Python code *Fluxi* from our research group, which was originally written by our former member, **Thomas Hümmer**. The main goal of the GUI was to provide a flexible tool for generating waveforms and configuring all relevant parameters, such as waveform characteristics, carrier signals, and other channel settings, with the added advantage of allowing real-time adjustments

during the experiments. It was also designed to be easily extensible, enabling the integration of further applications and compatibility with different AWG models via alternative Python interfaces. At the current stage, however, this GUI is no longer under active development and is now used exclusively with the complete AWG hardware within the optical cavity setup operated by another colleague.

For ensemble spectroscopy, the currently employed AWG from Quantum Machines does not include a dedicated GUI. Instead, it is programmed using the Python-based QUA package provided by the manufacturer. This package enables full control of pulse parameters and the generation of pulse sequences. In general, the control program is structured in two parts: a *configuration file*, where all relevant parameters are defined, and an *execution file*, which accesses these parameters to perform the pulse sequence of the corresponding measurement. Additionally, preexisting modules from our Fluxi programs, such as those developed for automated DAQ, can be readily integrated. The pulse sequences of the corresponding specific measurement protocols are precompiled and uploaded to the FPGA of the OPX+, where they are subsequently executed in loops according to the defined number of iterations. Furthermore, a library containing preprogrammed pulse sequences from other research groups is commercially available, providing a valuable resource for extending or optimizing custom program codes with minimal development effort.

3.3. Cryogenic environment

As already stated at the beginning of this chapter, there was no dedicated cryogenic setup available for ensemble spectroscopy. For this reason, home-built solutions were introduced and modified based on experience, which also required the sample preparation to be adapted. Several dipstick cryostats were used, some of which were upgraded with a cylindrical coil to implement an RF control, while a custom small-footprint *flange dipstick* was constructed for routine spectroscopic measurements or quick screening of new material samples. All of these cryostats are limited to the liquid-helium temperature of about 4.2 K, which is sufficient for most spectroscopic measurements, but many other effects or material properties can only be observed at even lower temperatures. For a few samples, we had the opportunity to perform additional measurements within two dilution refrigerators reaching temperatures down to 50 mK. A brief summary and description of all cryostats used within the scope of this work, including their key features and components, is provided below.

3.3.1. Dipstick cryostat

The so-called *dipstick cryostats* are a commonly adopted and cost-effective solution for performing cryogenic measurements, as they only require a commercially available helium dewar and a sample chamber designed to fit the geometry of the helium dewar neck, allowing it to be immersed in liquid helium. In addition, there are further major advantages, such as the ability to operate many of these dipstick cryostats in parallel, the low consumption rate of liquid helium, and the fact that modifications or upgrades can be implemented more quickly due to the lower complexity of this type of cryostat system. Among the various dipstick cryostats employed throughout this work, the first and longest-used setup is the *exchange gas dipstick*, which served as a fundamental system for most experiments and optimization efforts.

Exchange gas dipstick: The exchange gas dipstick, illustrated in Figure 3.6(a) and (b), consists of three main parts: the outer cylindrical tube, the inner rod mounting system and the six-way cross. The outer diameter of the cylindrical tube was designed to fit the *KF50 flange system*¹⁵, matching the standard neck diameter of most helium dewars. The tube was sealed at the lower end using a welded blind flange, while an adapter piece was welded onto the upper end to ensure compatibility with the six-way cross. The inner part serves primarily as the sample holder, consisting of a two-rod structure stabilized by four copper radiation shields. The shields are spaced about 20 cm apart. Originally, this dipstick cryostat was designed to incorporate an optical fiber-based microcavity at the lower end of the mounting system. As ensemble spectroscopy required a dedicated sample section, additional mounting systems were installed, as shown in Figure 3.6(b). The six-way cross was primarily used as an interface for electronics and fiber optics, while one port was always blocked for connecting the pump line. For the electronics, commercially available *D-Sub15*¹⁶ flanges were utilized to control two temperature sensors of the type *Cernox CX 1050 HT*¹⁷, and to drive piezos that are integrated into our cavity setup. One temperature sensor is located next to the cavity mount, and the second one is fixed on the sample holder stage for ensemble spectroscopy. The distance between both sensors is approximately 30 cm. To include *SubMiniature version A (SMA)* connectors or optical fibers, standard blind flanges were used and drilled to the required diameter. As the footprint of our samples is comparably small relative to the sample holder, more than one sample can be prepared and analyzed during one cooldown. The exchange gas dipstick is equipped with seven fiber feedthroughs in total, six of which belong to the ensemble spectroscopy, corresponding to a maximum of three sample spots, while only one was required for cavity experiments. Each sample requires two optical fibers: one for excitation and the other for signal collection. In order to guarantee vacuum-tight fiber feedthroughs, a two-component epoxy adhesive was used to fix the

¹⁵ Quick flange with 50 mm inner diameter.

¹⁶ Model: *KF50-SUBD-15-BASIC*, purchased from *VACOM*.

¹⁷ Model: *Cernox CX 1050 HT in CU package*, purchased from *Lakeshore*.

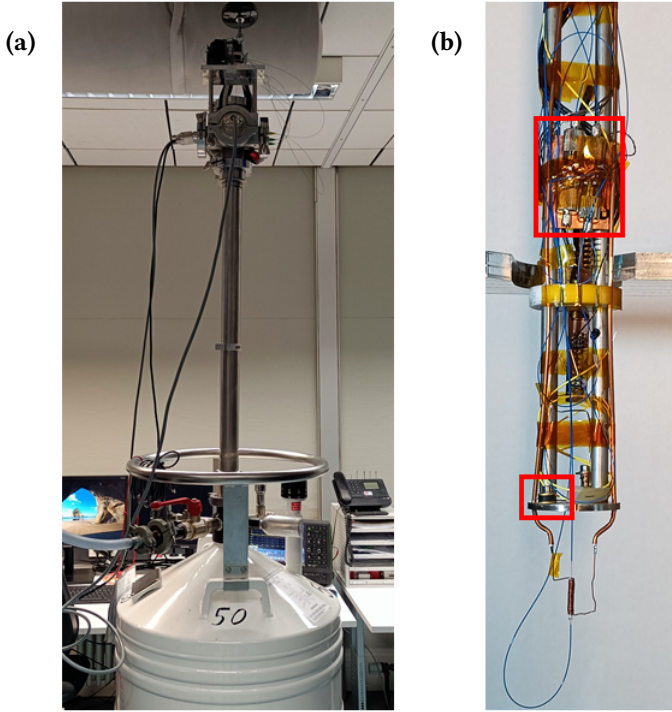


Figure 3.6: Exchange gas dipstick cryostat. (a) The dipstick cryostat consists of a cylindrical outer tube made of stainless steel, while the inner part is a rigid two-rod construction serving primarily as a sample holder for ensemble spectroscopy experiments. Fiber-optic and electrical access is realized via the six-way cross, which is attached to the top part of the tube. The dipstick in the image is shown during a cooldown period, where it is pushed into a dewar through the neck filled with liquid helium. Before cooling can be initiated, helium gas particles are introduced into the dipstick to act as a heat-exchange medium between the cooled walls of the tube and the inner mounting system, which incorporates the sample. (b) The lower end of the two-rod construction includes two temperature sensors (red solid boxes). One of them is located on the lower mounting stage, intended for optical cavity experiments, while the second one is positioned on a copper stage, to which all prepared samples combined with the fiber-based ferrule setup can be attached. Two exemplary ferrule systems are depicted on the mounting stage. At the lower end, an additional sample is integrated into an RF coil.

fibers in position and seal any remaining openings. Once all samples are prepared, the cooling process can be initiated. First, two *butterfly valves* are attached to the six-way cross in the open position. Then, a vacuum pump is connected, and the dipstick cryostat is evacuated to a pressure of approximately 10^{-4} mbar. Unfortunately, the welding seams were not sealed vacuum-tight, so that the pumped vacuum does not last too long, with a maximum duration of about two weeks. After reaching a sufficient vacuum, both butterfly valves are closed, the vacuum pump is disconnected, and a connection to the helium dewar is established. In the next step, boil-off helium from the helium dewar is

gradually introduced into the dipstick via the butterfly valves until a final pressure of about 1 bar of helium, which serves as the exchange gas, is reached. Finally, the dipstick cryostat is inserted step by step into the helium dewar up to the point at which both temperature sensors indicate the liquid helium temperature of 4.2 K. Although the local temperature at the sample may vary during excitation or when the sample is placed inside holders made of materials with low thermal conductivity, the thermalization using a helium exchange gas is generally considered highly reliable. The helium atoms cool the inner part of the cryostat and, thus, the sample itself through heat exchange with the cooled walls. During the cooldown and measurement phases, the helium dewar is connected to a helium return line, allowing the majority of the boil-off helium to be recovered via a closed-cycle loop and redirected back into the helium reservoir in the helium hall of the *Physics Institute*. With a usual consumption rate of 1 L to 2 L per day, the operational time can extend up to three weeks without warming up the dewar [62].

Transfer tube dipstick: This dipstick, inherited from the previous research group of **Professor Georg Weiß**, is a modified helium transfer line, which has been adopted for use in our experimental setup. Figure 3.7(a) shows the transfer tube dipstick in its upgraded form, inserted into the helium dewar during experimental operation. The major advantage of this design is that the sample holder is in direct contact with the liquid helium, enabling optimal thermalization at 4.2 K. At the upper end of the tube, a small box is mounted to incorporate various electrical feedthroughs, e.g., for MW control, which lead down to the sample holder. For our purposes, optical fiber feedthroughs were added and vacuum-sealed at the top of the transfer line, while the existing electrical connections were not utilized in this setup. The helium consumption for this dipstick is also very cost-efficient, with measurement periods of three weeks requiring about 60 L to 70 L of helium [62].

Flange dipstick: As the name suggests, this extremely simple design is based on a standard KF50 flange. Depending on the number and size of required feedthroughs, multiple optical fibers and electrical connections can be installed. Accordingly, all feedthroughs and sample holders must be cryo-compatible, since in this case as well, the inserted components come into direct contact with liquid helium at 4.2 K. The optical feedthroughs are sealed using the same method and two-component epoxy adhesive described above, whereas the electrical interface is introduced by SMA connectors, which are tightened and thus pressed against the flange to ensure a vacuum-tight seal. Currently, many such flanges equipped only with optical fibers are in use, as they enable both quick sample exchange and efficient sample characterization. The design and follow-up modifications of the sample holder are introduced in Section 3.4. However, the required optical fibers are standard commercially available multimode fibers¹⁸. In

¹⁸ Purchased from *Thorlabs*.

3. Experimental setup

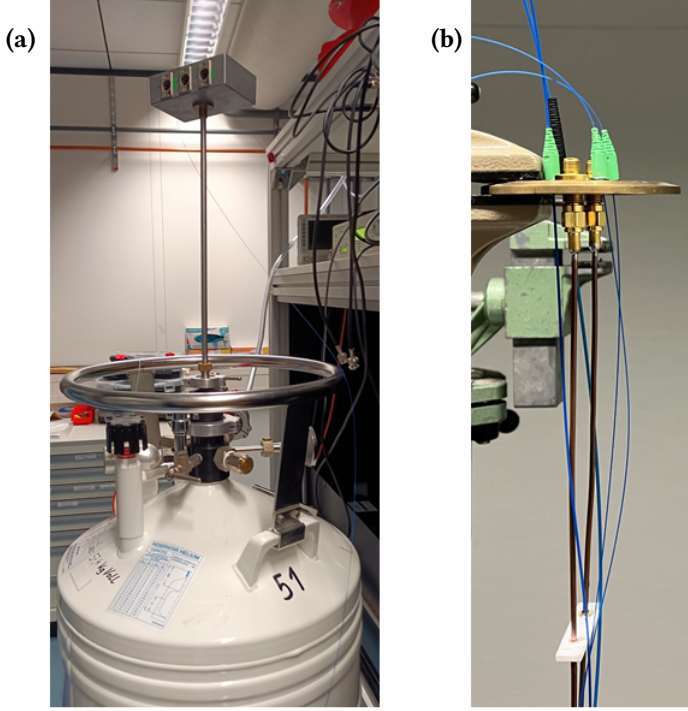


Figure 3.7: Transfer tube and flange dipstick cryostats. Both dipsticks, including the integrated samples, are directly immersed in liquid helium, providing optimal thermalization. **(a)** For the transfer tube, fiber feedthroughs were added and vacuum-sealed at the upper end of the transfer line, so that the fibers run inside the tube and only the sample mounted at the lower end is inserted into liquid helium. **(b)** The flange dipstick represents the simplest of our designs. Electrical and optical connections are implemented through feedthroughs in a standard blind flange. The image shows two semi-rigid coaxial RF lines connected via SMA connectors, primarily contributing to mechanical stability, as well as glued and sealed optical fibers using an epoxy adhesive. In this configuration, all components are exposed to liquid helium. The RF lines feature an outer conductor made of copper to minimize the thermal load during operation of the RF coil.

total, the following three fiber models were used, differing primarily in their overall and core diameters:

1. **FP200ERT**: 0.5 numerical aperture (NA), $(200 \pm 5) \mu\text{m}$ core diameter, $(500 \pm 30) \mu\text{m}$ coating diameter, step-index multimode fiber.
2. **FP600ERT**: 0.5 NA, $(600 \pm 10) \mu\text{m}$ core diameter, $(1040 \pm 30) \mu\text{m}$ coating diameter, step-index multimode fiber.
3. **FP1000ERT**: 0.5 NA, $(1000 \pm 15) \mu\text{m}$ core diameter, $(1400 \pm 50) \mu\text{m}$ coating diameter, step-index multimode fiber.

At first consideration, the term *dipstick* may appear inappropriate for the general flange design. Nevertheless, with the implementation of a cylindrical RF coil, two semi-rigid coaxial cables were connected to the SMA connectors on the flange, allowing the coil to be positioned and soldered at the lower end. As a result, the setup once again resembled a *classic dipstick* configuration, as illustrated in Figure 3.7(b). The semi-rigid coaxial cables¹⁹ were originally purchased for use with the exchange gas dipstick. Since their outer conductor is made of copper, the intention was to enhance thermalization, as high RF powers could introduce significant heat. In the case of the flange-based dipstick, however, thermalization of the coaxial lines is not expected to represent a major challenge. The cable length was chosen to be approximately 1 m, taking into account the geometry of the helium dewar, which has a total depth of about 1.113 m. In this configuration, the coil is positioned just above the bottom of the dewar. To provide additional mechanical stability, three Teflon components were attached equidistantly along the coaxial cables at distances of ≈ 30 cm using cryo-compatible adhesive. Additionally, the optical fibers can be fixed to the coaxial cables to reduce the risk of damage, which is comparatively higher in the standard flange-based cryostats without any fiber mounting options. The coil design was tailored and adapted to match our sample holder structure, such that during operation, the sample remains positioned inside the coil.

Implementation of RF control: In order to enable full coherent control of the Eu^{3+} nuclear spin, a dedicated RF infrastructure is required. Our RF setup is based on the concept used at the University of Geneva in the research group of **Mikael Afzelius**, which has been implemented in several previous PhD theses [76, 98, 99]. Figure 3.8 shows the schematic layout of our RF setup, which consists of a signal-generating device (OPX+), a cylindrical coil, impedance matching electronics, a high-power amplifier²⁰, and various attenuators to prevent any damage occurring from power reflections. Since we use custom-designed sample holders, their geometry primarily determined the inner diameter and number of turns of the RF coil, ensuring that the sample is fully enclosed by the coil during operation.

The general resonance frequency ω_0 of an LC circuit is given by [100]:

$$\omega_0 = \frac{1}{\sqrt{LC}}, \quad (3.3.1)$$

with L representing the inductance of the coil and C the capacitance of the capacitor within the circuit. The inductance L of the RF coil can be calculated from its geometry. For an *infinitely* long cylindrical coil, the inductance is described by the following equation [100]:

$$L = \mu_0 \mu_r \frac{N^2 A}{l}, \quad (3.3.2)$$

¹⁹ Model: PECX005, purchased from MRC Gigacomp.

²⁰ Model: BSA 1025-150, purchased from BONN Elektronik.

3. Experimental setup

where μ_0 is the vacuum permeability, μ_r the relative permeability of the core material (typically 1 for air), N the number of turns, A the cross-sectional area of the coil, and l the length of the coil. This expression assumes an idealized coil of infinite length, neglecting edge effects and the geometry of the wire. In most practical or realistic implementations, including the RF coils used in this work, the coil length is finite and often of the same order of magnitude as its diameter. To account for this, a more accurate approximation includes a correction factor that depends on the ratio of the coil diameter D to the coil length l [100]:

$$L \approx \mu_0 \mu_r \frac{N^2 A}{l} \cdot \frac{1}{1 + 0.45 \frac{D}{l}}. \quad (3.3.3)$$

More detailed considerations, such as specific diameter-to-length ratios or multilayer windings, can be found in the work of Wheeler and Dobbie [101]. In such cases, alternative approximation formulas may provide a better fit and include additional effects, such as the coil thickness in multilayer configurations.

Once the inductance L is known, the required capacitance C for a desired resonance frequency ω_0 to match at least one of the hyperfine transitions can be determined using the resonance condition in Equation 3.3.1. It should be noted that any single coil also exhibits a parasitic self-capacitance, which depends on its geometry and must be considered to estimate the total effective capacitance and tuning range of the circuit. A widely used empirical estimate for the self-capacitance of a single-layer air-core coil was proposed by Medhurst [102]:

$$C_s = 0.46 \cdot D, \quad (3.3.4)$$

with D being the coil diameter in centimeters and C_s the resulting self-capacitance in picofarads. This approximation holds reasonably well for coils with aspect ratios of $0.5 < l/D < 2$, although the underlying physical explanation remains debated. On the basis of a careful analysis of self-capacitance measurements performed on a large number of coils, Medhurst derived a semi-empirical formula, which is valid for a broader range of coil geometries regarding the l/D ratio.

Using a vector network analyzer (VNA), the resonance of the LC circuit can be observed and characterized. As illustrated in Figure 3.8(a), two variable capacitors were integrated into the circuit: the parallel capacitor allows tuning of the resonance frequency, while the series capacitor adjusts the width of the resonance and thus affects the quality factor Q of the LC circuit. The combination of both capacitors and the RF coil is designed to match the overall circuit impedance to $50 \, \Omega$. The use of tunable capacitors enables dynamic adjustment of the coil resonance for different experimental conditions or samples.

As part of this work, two RF coils were self-wound using copper-stabilized multifilament NbTi superconducting wire ²¹ with an insulated diameter of 0.43 mm. This material

²¹ Model: 54S43, manufactured by SUPERCON and provided by Professor Wolfgang Wernsdorfer.

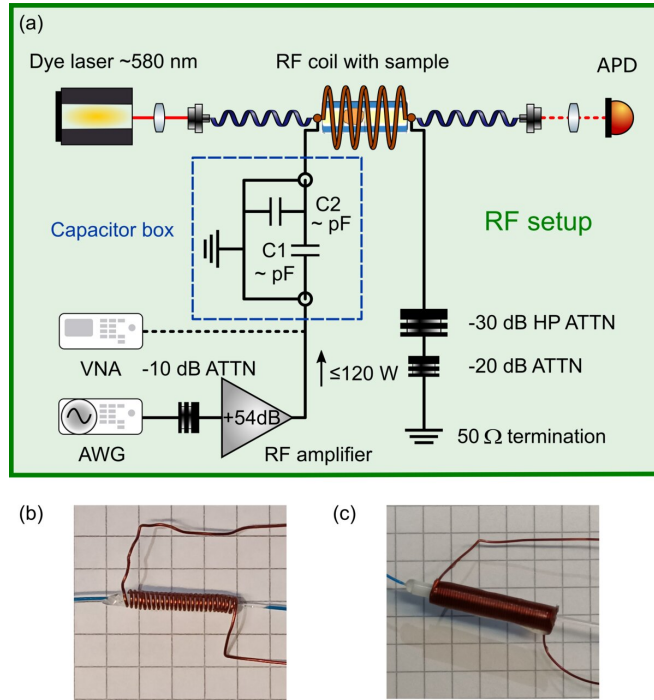


Figure 3.8: Overview of the RF infrastructure. (a) The diagram illustrates how the generated RF signal is guided to the coil and exposed to the sample, showing components such as the high-power RF amplifier, attenuators (ATTN), transmission lines, and a 50 Ω matching circuit annotated with their respective gain and attenuation factors. The signal is generated via an AWG and then directed to a power amplifier, while passing through an attenuator to protect the setup from potential damage due to reflected signals. It then enters a 50 Ω capacitor-based matching circuit (dashed blue box), which, in combination with the RF coil, allows tuning of the resonance frequency, bandwidth, and depth of the resonance by adjusting series- and parallel-connected capacitors (on the order of picofarads). In typical measurements, RF power levels ranged from several hundred milliwatts up to about 100 W. To attenuate such powers, a high-power attenuator (HP ATTN) is connected directly to the output of the coil, followed by conventional smaller attenuators, before the circuit is terminated with a 50 Ω end connector. Optionally, a VNA can be connected to monitor the resonance characteristics in real time, which is particularly required when adjusting to the hyperfine levels of the corresponding sample. The figure is adapted from [99], and was created with Inkscape and the Component Library [93]. Images (b) and (c) show the two custom-built RF coils used in this thesis. The coil dimensions are on the centimeter scale, as indicated by the millimeter grid paper in the background. Image (b) shows an air-wound coil with spaced turns, while in (c) the turns are closely packed and fixed in position with an epoxy adhesive coating to ensure a stable coil geometry.

becomes superconducting below 10 K, ensuring compatibility with liquid-helium temperatures and minimizing the thermal load. The primary sources of heat input are the solder joints of the RF coil and the non-superconducting coaxial feed lines. Both coils are shown in Figure 3.8(b) and (c). The first coil features undefined air gaps between the windings, whereas the second coil was encapsulated with a two-component epoxy adhesive, resulting in direct contact between the windings and thus enhanced mechanical stability. The coils were fabricated sequentially, and the epoxy-embedded coil is currently in use for the experiments. Further details regarding the coil geometry, key parameters, and corresponding calculations are provided in Appendix B.

3.3.2. Dilution refrigerator

In contrast to the previously discussed cryostats, the dilution refrigerator forms the central device of ultra-low-temperature experiments, providing operational temperatures down to the millikelvin regime. The major working principle is based on the dilution process of ^3He in ^4He . Although such systems are particularly complex and exhibit a higher need for maintenance, the thermal stability and available functionalities in the sample chamber are beneficial for high-sensitivity optical and spin-based measurements. In terms of enhancing the coherence properties, REIs in solid-state hosts definitely require temperatures in the millikelvin range, as many interactions, which are discussed in Subsection 2.2.2 of Chapter 2, feature a temperature dependence and thus can be minimized or even suppressed.

Sionludi cryostat: The dilution refrigerator used in this work is a commercial cryostat, developed and sold by the startup *Qinu*, originating from the research group of **Professor Wolfgang Wernsdorfer** at the *Physics Institute*. The model *Quinu version LPO* [103], which is illustrated in Figure 3.9, was specifically customized to meet the experimental requirements of our different setup configurations. In the following, we will refer to it as the *Sionludi*, being the general internal name at the institute. In contrast to other commercial systems, this cryostat is a table-top cryogenic platform employing an *inverted* configuration, such that the coldest component is located at the top of the setup. The Sionludi cryostat is specifically designed for fast cooldowns within 6 h, operation at millikelvin temperatures (specified to about 30 mK), and low-vibration experiments conducted on optical tables.

The cooling process involves many complex steps and requires a deeper understanding of the overall structure of the cryostat. Specific details on the Sionludi and its internal physical processes can be found in the theses of **Alexander Zilz** and **Ioannis Karapatzakis** [11, 104]. Here, we only elaborate on the fundamental basics of the design and the working principle. The Sionludi consists of four vertically stacked thermal stages, each of which is responsible for stabilizing the local temperature at a constant value during the cooldown. The bottom stage constitutes the 100 K temperature level, followed

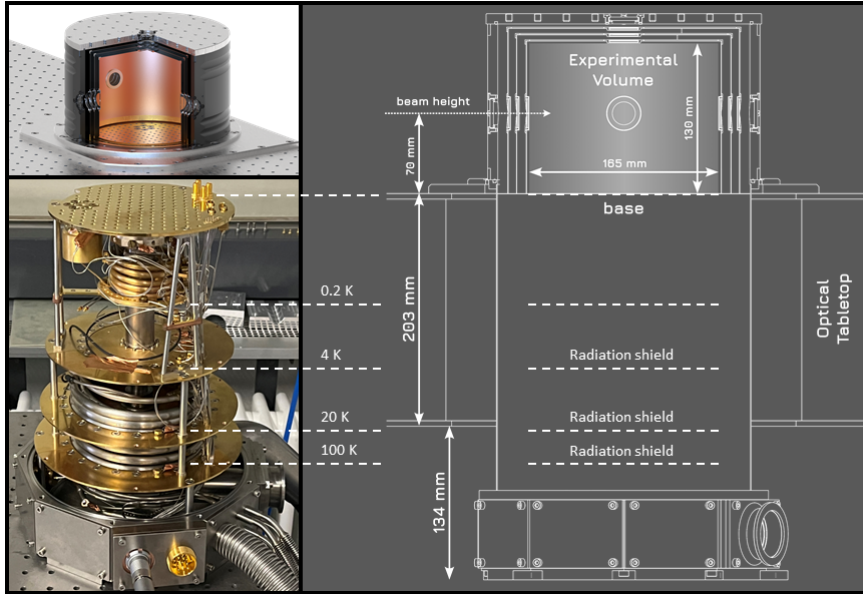


Figure 3.9: Schematic overview of the Qinu LPO cryostat. The table-top Qinu cryostat is a dilution refrigerator, which is primarily designed for low-noise optical experiments reaching cryogenic temperatures below 100 mK (specified to approximately 30 mK). Compared to other commercial dilution refrigerators, these types of cryostats employ an inverted configuration, so that the base plate, at which the millikelvin temperatures are provided, is at the top of the setup. This version of the cryostat consists of several different thermal stages, which are connected via two closed-cycle heat exchanger circuits. The first one is a pure ^4He loop in order to precool the system to about 4.2 K using liquid helium provided by a pulse-tube refrigerator. The second circuit employs a $^3\text{He}/^4\text{He}$ loop, which enables continuous cooling down to the millikelvin regime. The cooling power is provided by the heat resulting from the dilution of both helium isotopes. The thermal isolation between the different stages is realized through low-conductivity mounts made out of stainless steel and three radiation shields attached to the 4 K, 20 K, and 100 K plates, followed by a final vacuum shield. Optical access is guaranteed either via fiber feedthroughs or via free-space access through side and top windows installed on all radiation and vacuum shields, with three windows on the sidewalls and one on the top part of each shield. In addition, several electrical connections are provided to enable external control of optical cavity setups and to implement RF control for future experiments. The upper left and the right pictures are taken and adapted from [103].

by the 20 K, 4 K, and millikelvin thermal stages, while the latter one serves as the sample mount. In order to generate the respective temperature gradients, all thermal plates possess an individual amount of required connections to the heat exchangers at different positions. Thermal isolation between the stages is achieved through low-conductivity stainless-steel mounts and thermal shields made of copper, which are attached to the 100 K, 20 K, and 4 K plates, preventing heat exchange via radiation. An additional fourth shield serves as the vacuum shield. The cooling system within the cryostat includes

3. Experimental setup

two closed-cycle heat exchanger loops, which both incorporate several transfer lines, enabling primarily cooling of the cryostat and, moreover, precooling of fresh incoming cryogenic fluids by utilizing transfer lines in a counterflow direction. While the main cooling cycle is supplied with liquid ^4He from a pulse-tube refrigerator to precool the cryostat at about 4.2 K, the cold plate is subjected to the $^3\text{He}/^4\text{He}$ cooling cycle, enabling further cooling to millikelvin temperatures via the dilution refrigeration process. For the purpose of understanding, a cross-sectional schematic overview of the cryostat is provided in Appendix C [11, 104].

The sample chamber features a gold-coated cold plate with a diameter of 160 mm and a total height of 130 mm, which is sufficient to incorporate optical cavity setups together with our small-footprint sample holders for the ensemble spectroscopy. In addition, the cold plate includes 59 electrical and eight optical fiber feedthroughs, of which four were used for our ensemble spectroscopy and the remaining ones for the cavity setups. The base temperature is specified to reach temperature values less than 30 mK. For this reason, cooling occurs via thermal conduction, provided that thermalization is properly established. The cooling power of the cryostat is highly dependent on the operating temperature mode, the specification at 100 mK is 200 μW . For the purpose of free-space excitation, the vacuum shield and each of the three radiation shields possesses three optical fused-silica windows on the sidewalls and one on the top end of each shield (outer windows: 2 mm thick, inner windows: 1 mm thick).

Cryogenic confocal microscope: The second Sionludi used within the scope of this thesis is based on an older model compared to our modified *Quinu* cryostat. Figure 3.10 and the schematic overview shown in Figure C refer exactly to this model. However, the working principle for both versions remains the same. In particular, this setup provides the possibility to perform confocal microscopy at desired cryogenic sample temperatures. The sample mount includes a copper holder and a scannable three-axis commercial positioning stage ²², which is attached to the cold plate. As shown in Figure 3.10, the sample holder is rather suitable for macroscopic or platelet-like crystals. Initially, the sample is fixed by a thin layer of poly(methyl methacrylate) (PMMA) on a silicon wafer chip, which then is glued onto a copper plate. The silicon wafer is a highly absorbing material in order to prevent parasitic fluorescence contributions. Since the cryostat is equipped with electrical RF and MW feedthroughs, a wire bond can be placed over the sample, as illustrated in Figure 3.10, to introduce coherent spin control. Finally, the sample is mounted on top of the positioning system, and the copper holder can be attached to silver strands, allowing further improvement of the thermalization. On top of the radiation shield for the 4 K plate, a copper mounting bracket is installed, into which a high-NA objective ²³ can be screwed. Optical access to the cryostat is realized through a fused-silica window within the top part of the vacuum

²² Model: two ANPx101/Res/LT positioners, one ANPz101/Res/LT positioner, and one ANC300 controller, purchased from Attocube.

²³ Model: Olympus MPLN100X with 0.9 NA.

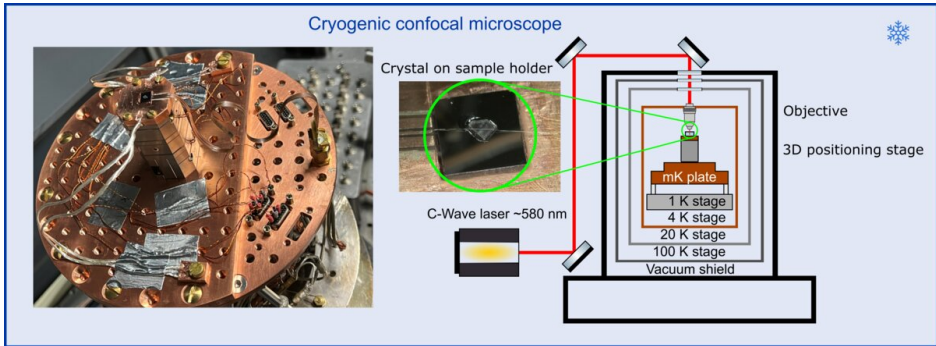


Figure 3.10: Cryogenic confocal setup within the Sionludi cryostat. The left part of the image shows the copper base plate of the cryostat, onto which a commercial three-axis positioning system is mounted. The sample holder is fixed onto the positioning system and thermally anchored to the millikelvin stage via additional silver braids. This system is essential both for adjusting the sample height with respect to the focal point of the objective and for enabling spatially resolved investigations across the sample. Normally, a copper construction incorporating the high-NA objective is placed on top, serving as a radiation shield at the 4 K stage. However, it has been removed here for clarity to better visualize the setup and the sample. The positioning system, and thus the sample, are thermally separated from the objective. The schematic on the right highlights the different thermal stages, which can be identified by their corresponding radiation shields (4 K, 20 K, and 100 K), as well as a vacuum shield. Optical access is provided through top windows in each shield, allowing the excitation light to be focused onto the sample via the objective. The inset shows a prepared sample, consisting of a macroscopically grown crystal glued onto a silicon chip, which is in turn mounted on a copper holder. Additionally, a wire was bonded across the sample, intended for coherent spin control in future experiments. The emitted fluorescence is collected through the same objective and can be detected either by an APD or a spectrometer. The figure is adapted from [105] and was created with Inkscape and the Component Library [93].

shield and small apertures in each thermal shield. The optical setup of the implemented confocal microscope is based on conventional principles and can be compared to the existing confocal setup in the research group of **Professor David Hunger**. For detailed descriptions on the overall setup and the working principle, we refer to the thesis of **Ioannis Karapatzakis** [11]. Off-resonant and on-resonant excitation light at 532 nm²⁴ and 580 nm²⁵, respectively, can be guided through the objective and focused onto the sample. The emitted fluorescence is then collected by the objective and directed via a 90:10 (ratio of T : R) beam splitter to the detection path. The fluorescent light can be spectrally filtered by using a filter block in order to tailor the required wavelength range and to remove the excitation light. In a final step, the filtered light is focused through a pinhole²⁶ and sent either directly to a single-photon counting module²⁷ or via a flip

²⁴ Model: *Ventus MPC6000*, purchased from *Laser Quantum*.

²⁵ Model: *C-Wave*, purchased from *Hübner Photonics*.

²⁶ Model: *P30HK*, purchased from *Thorlabs*.

²⁷ Model: *SPCM-AQRH-16*, purchased from *Excelitas*.

mirror to a commercial spectrometer²⁸ [11, 105]. This cryogenic confocal setup allows the measurement of many characteristic optical properties of our Eu^{3+} -based samples in a subensemble regime, since the focal spot size of the excitation light is on the order of $1\text{ }\mu\text{m}$, compared to conventional ensemble spectroscopy. The wire bond was not used, but can be applied for future coherent RF control experiments in this configuration.

3.4. Description of fiber-based ferrule sample holder

Our current design of the fiber-based ferrule sample holder is the result of empirical and collective efforts, including particularly the work of **Xiaoyu Cheng**, **Christina Ioannou**, and **Vishnu Unni C.**. As several measurement techniques require different sample morphologies, the sample holder was reproduced in many modified configurations, while the working principle remained the same. The central advantage of this sample holder is that most individual parts are commercially available at *Thorlabs*, and only specific supplementary components were produced in the mechanical workshop of the *Physics Institute*. As shown in Figure 3.11(a), the basic arrangement of the sample holder consists of two opposing ferrules, incorporating multimode fibers (see Subsection 3.3.1) for both sample excitation as well as signal collection, and a fiber casing to which both ferrules can be attached.

1.) CO₂ laser machining and lithography: In the first iteration, the sample volume was fabricated via CO₂ laser machining as a conical shape into one of the fibers [91], with the other fiber remaining unchanged. This fabrication process required afterwards additional post-processing lithography steps, and was not reproducible at all, resulting in small sample volumes, poor collection efficiencies, and fewer iterations conducted for sample preparation. The conical depression was initially created on a single-mode fiber, serving as the excitation fiber, while the unprocessed fiber was always of multimode type²⁹. After laser machining was omitted, the sample space was realized by pulling back the single-mode fiber inside the ferrule by a constant distance of approximately $200\text{ }\mu\text{m}$ from the front surface. The exact movement of the fiber during the adjustment process can be controlled with the help of a micrometer translation stage and a white-light interferometer (WLI). Both approaches described here involve physical vapor deposition in order to create a silver coating layer with a thickness of a few hundred nanometers within the sample space of the ferrule. Although the post-processing lithography could be successfully performed, the measured collection efficiency, or more specifically the ratio between incoming and outcoupled light from the fiber, was not suitable for experiments, when the sample was integrated into the ferrule [57].

²⁸ Model: *SP-2500i*, purchased from *Princeton Instruments*.

²⁹ Model: *GIF-625* with 0.275 NA , $(62.5 \pm 2.5)\text{ }\mu\text{m}$ core diameter, $(245 \pm 10)\text{ }\mu\text{m}$ coating diameter, graded-index multimode fiber, purchased from *Thorlabs*.

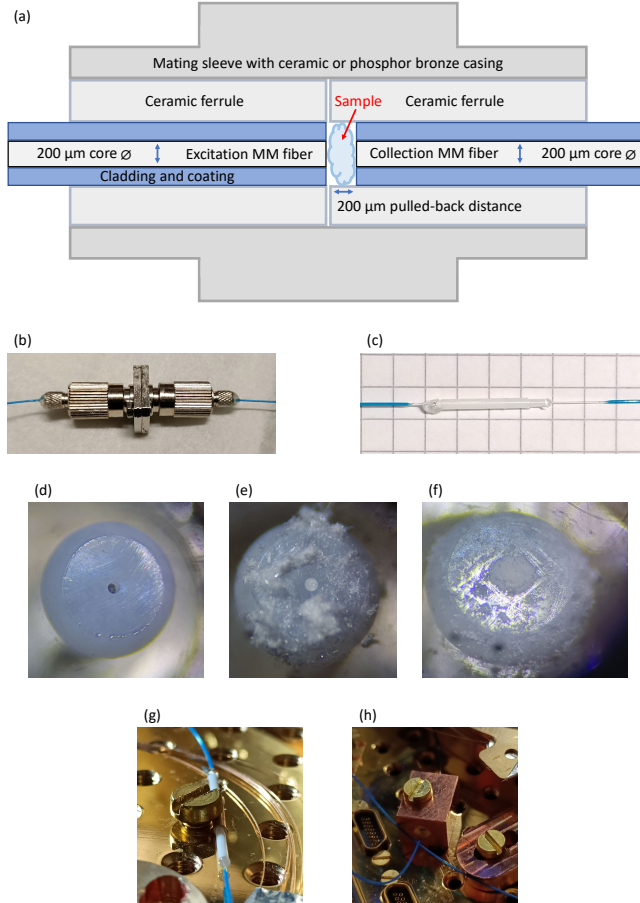


Figure 3.11: Design and modifications of the fiber-based ferrule sample holder. (a) In general, a sample holder consists of two multimode fibers with a core diameter of $200\ \mu\text{m}$, each glued into separate ferrules, where one fiber is used for excitation and the other for collection. One fiber extends fully to the end surface of the ferrule, while the second is pulled back by a distance of about $200\ \mu\text{m}$, forming a small volume between the fiber ends that serves as the sample chamber. The approach in (b) shows a version, where the ferrules are integrated into commercial fiber connectors that are coupled via a mating sleeve. In contrast, the sample holder in (c) employs only bare ferrules and a ceramic housing to incorporate them, representing a small-footprint alternative. Images (d), (e), and (f) illustrate the filling process of powder-based samples, which is carried out iteratively by filling and compressing the material using a mini-spatula or an auxiliary fiber. The sample holder modifications (g) and (h) represent designs intended for integration into the dilution refrigerator, as they are made from materials with high thermal conductivity. In (g), a standard ferrule setup is mounted inside a phosphor bronze casing, while (h) uses a solid copper block as a substitute for the ferrules, with a single through-hole drilled for the multimode fibers. To further improve thermalization, the sample holders are tightly screwed onto the base plate.

2.) Multimode pulled-back principle: As the collection efficiency could not be improved, the silver coating process was also omitted. Nevertheless, the resulting cylindrical sample volume, introduced by the pulled-back fiber configuration, exhibits a higher load capacity for the sample and facilitates sample preparation. Most of the samples feature a powder-like structure with grain sizes ranging from a few tens of nanometers up to several millimeters, while the latter size corresponds to rather macroscopic crystals. Small powder samples constitute a highly scattering medium, which is the primary reason for the low collection efficiencies. For this purpose, the single-mode and multimode fibers were exchanged for another type of multimode fiber (see Subsection 3.3.1) with a larger core diameter and higher NA to primarily increase the excitation and collection area. Both fibers are then glued into the corresponding ferrules using an ultraviolet-curing optical adhesive ³⁰: the first multimode fiber utilizes the pulled-back principle, and the second fiber is flush with the end facet of the ferrule. In Figure 3.11(b) and (c), it can be seen that the ferrule is either integrated into a commercial fiber connector ³¹ or is available as a bare part ³². This iteration of the pulled-back sample holder mostly employed integrated ferrules, which can be connected with each other by using a fiber mating sleeve ³³. Finally, a significant improvement in the collection efficiency could be achieved, with values of about 0.1 %, which is two orders of magnitude higher compared to the previous approaches. At this point, the sample holder represents a reproducible and small-footprint device with an overall size of a few centimeters, enabling both quick sample preparation and sample exchange [57].

3.) Optimization of pulled-back sample holder: Although the modified design led to substantial progress in the experimental results, the signal quality and the integration into different cryogenic setups required further improvement in sample preparation and slight adjustments to the sample holder, respectively. The analysis of previous measurements revealed that the collected signal was close to the noise level, indicating a deficiency in the amount of sample used, which corresponds physically to less optical depth. For this reason, the filling procedure of the samples was then monitored under a microscope. The ferrule containing the pulled-back multimode fiber is fixed vertically on a fiber mount. A mini spatula is utilized to pick up the crystal grains in the form of a powder and place them on top of the surface of the ferrule. Afterwards, the powder can be moved into the borehole of the ferrule, which, in the case of the 200 μm core diameter multimode fiber, is about 230 μm wide. Repeating this step three to four times results usually in a completely filled borehole, which can be finally compressed with the flat side of the mini-spatula or an auxiliary fiber. Figure 3.11(d)–(f) illustrates the ferrule before and during the filling procedure of the powder sample [62]. During the integration of the ferrules into the casing or mating sleeve, some powder may fall out. Therefore, additional powder is deposited on top of the pulled-back ferrule

³⁰ Model: *Norland Optical Adhesive 63*, purchased from *Thorlabs*.

³¹ Model: *30230C1*, purchased from *Thorlabs*.

³² Model: *CFX230*, purchased from *Thorlabs*.

³³ Model: *ADAF1*, purchased from *Thorlabs*.

at the end of the filling process to compensate for potential losses and to improve compression. Only with this preparation method did the collection efficiencies reach values slightly above 1 %, which was sufficient to detect transmitted signals through the pulled-back fiber-based sample holder with enhanced quality, including strong absorption. In cryostats, where the sample holder is directly subjected to liquid helium, the thermalization is not significantly affected by its geometry or the materials of the built-in components. For cryostats with exchange gas or thermally conducting cold plates, a modified version of this sample holder was produced using a phosphor bronze casing³⁴ in which only the bare ferrules with the multimode fibers are fixed by a two-component epoxy adhesive, as depicted in Figure 3.11(g) [62]. To create a thermal contact, the phosphor bronze casing is pressed onto the cold plate via a brass screw. The commercially available ferrules at *Thorlabs* are either made of ceramic or stainless steel, which both do not feature a suitable thermal conductivity. Figure 3.11(h) illustrates our custom-designed copper ferrules, machined by our mechanical workshop, with the purpose of improving the thermalization and establishing a universal sample holder which fits into most cryostat configurations. However, an exact conclusion could not be made, as the individual parts contained small mechanical defects and, in some cases, the precise requirements on the production process were technically unfeasible, adversely affecting our preparation method.

4.) Asymmetric fiber configuration: The latest design upgrade was required for incorporating macroscopic crystalline platelets combined with the pulled-back scheme. While the usual borehole diameter and depth of the sample volume are intended for the use of powders, randomly sized macroscopic crystals up to the millimeter range require different ferrule geometries. The quickest solution involves replacing the pulled-back multimode fiber and the corresponding ferrule with new versions featuring a larger fiber core diameter (up to 1 mm), which consequently requires a larger ferrule borehole diameter. Both components (see Subsection 3.3.1) are commercially available and can be easily substituted within the sample holder arrangement. In this configuration, the pulled-back multimode fiber serves as the collection fiber, while the standard fiber is used for excitation. Due to the larger core diameter, excitation through this fiber would result in reduced signal collection efficiency. Figure 3.12(a) represents the schematic layout of the asymmetric fiber configuration of the sample holder. Unfortunately, the ferrule with such a wide borehole is only available as part of a connector, as depicted in Figure 3.12(b), and this complicates the integration of the modified sample holder into the RF coil. The initial measurements with the RF coil were performed using a powder sample prepared within the previous configuration shown in Figure 3.11(c), involving bare ferrules and a casing. To prevent eddy currents or short circuits, the materials of the sample holder should be non-metallic. For 200 μm core diameter fibers, there are both ceramic ferrules and casings available. However, bare ferrules with larger borehole diameters had to be machined in our mechanical workshop. While ceramic is a hard

³⁴ Model: ADAL4-5 or ADAF4-5, purchased from *Thorlabs*.

3. Experimental setup

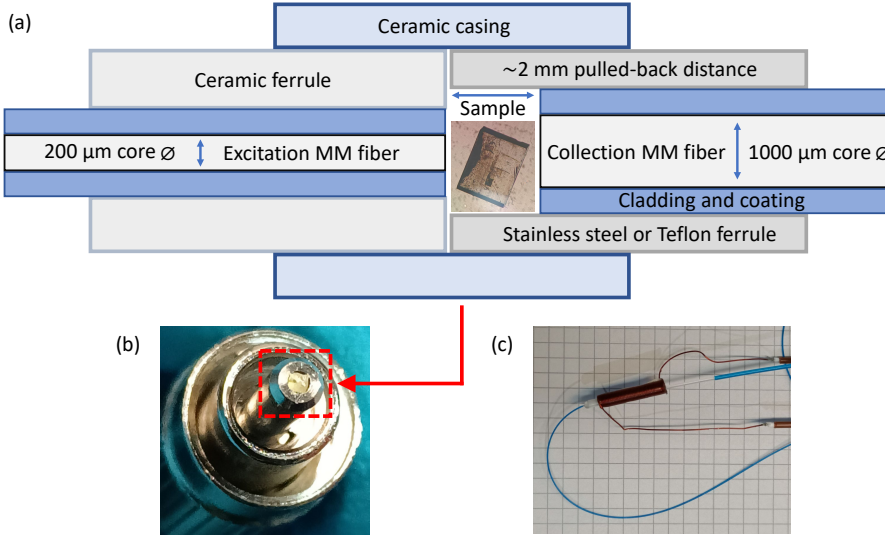


Figure 3.12: Asymmetric fiber configuration of the sample holder. (a) The asymmetric configuration represents a modification of the standard fiber-based ferrule sample holder, intended to enable the investigation of macroscopic samples. For this purpose, the pulled-back ferrule with the fiber was replaced by a version that accommodates crystals on the millimeter scale. The current model uses a multimode fiber with a core diameter of 1000 μm . In this design, the standard fiber (200 μm core diameter) serves as the excitation fiber, while the pulled-back multimode fiber is used for signal collection, thereby improving the transmission signal collection efficiency. Both ferrules can either be inserted into a ceramic casing or, if fiber connectors are utilized, connected via a mating sleeve. Image (b) shows a fiber connector with an integrated macroscopic crystal. Since commercial ferrules for fibers with such large core diameters are typically only available as fiber connectors with stainless steel ferrules, custom Teflon ferrules were fabricated for the sample holders to facilitate their integration into the RF coil. Image (c) shows the implemented asymmetric configuration in our RF setup, where a ceramic and a Teflon ferrule are inserted into a ceramic casing to avoid unwanted effects that can occur when metallic parts are placed inside RF coils.

material to drill, a feasible non-metallic material choice to process is Teflon. The distance from the edge surface of the Teflon ferrule was roughly adjusted to 2 mm without using the WLI, leaving enough space to fit different sizes of crystals. In this case, the sample preparation is not very accurate, since the crystal is placed inside the sample volume in a random position. Due to the differences in the stiffness of the materials, the sample holder required more gluing points for creating a rigid and stable device. The large core diameter of this new version of the multimode fiber influenced the final geometry of the sample holder and thus the RF coil with an inner diameter of 2.5 mm, as small-sized ferrules with an outer diameter of 1.25 mm were neither large enough to incorporate these fibers nor the macroscopic crystals. For this reason, the first wound RF coil (see Subsection 3.3.1) could not be reused and was replaced by the most current one, which is

depicted in Figure 3.11(c) together with the asymmetric pulled-back fiber configuration. Based on initial observations, this asymmetric sample holder arrangement has proven to be very promising, as well-grown macroscopic crystalline platelets are a less scattering medium than powder samples, so that the final placement of the material to be examined is not overly critical and yields reliable data quality for both optical and RF-driven measurements. Although the sample holder and measurements worked out successfully, these efforts can be seen as a proof of principle and require an even more systematic approach in the next step.

4. Ensemble spectroscopy of Eu^{3+} -based molecular complexes

Optically addressable, spin-bearing molecular systems are increasingly being investigated as promising quantum systems. This growing interest is primarily driven by the fact that molecules offer an exceptional degree of tunability through chemical engineering, enabling targeted control over material properties. Established quantum systems such as REIs can be embedded into tailored molecular environments that may offer more favorable conditions for the improvement of coherence characteristics than traditional solid-state hosts. Initial results have already demonstrated that the optical properties of several molecular compounds are highly promising, with optical coherence times reaching up to $10\ \mu\text{s}$ [1]. However, for the realization of practical quantum technologies such as quantum memories, further improvements of the optical coherence times are essential. In this regard, the electronic or nuclear spin, as in the case of Eu^{3+} , offers a valuable possibility to implement coherent control.

Currently, one of the main challenges though is the limited spin coherence reported for molecular systems [35], where electron spin coherence times have typically remained around $10\ \mu\text{s}$ to $20\ \mu\text{s}$, which is clearly insufficient for most quantum information applications. At the time of this work, nuclear spin manipulation combined with optical initialization and readout had not yet been realized in molecular systems. Only a few recent examples, such as the work from the research group of **Professor Joris van Slageren**, have achieved significantly extended electron spin coherence times, reporting up to $148\ \mu\text{s}$ below $100\ \text{K}$ in chlorinated triphenylmethyl organic radicals [106]. The primary goal of this chapter is to provide a systematic analysis of several Eu^{3+} -based molecular complexes, which demonstrates their suitability as quantum systems.

This chapter begins with a brief theoretical discussion of the mechanisms relevant in REI-based molecular systems, followed by a detailed overview of the spectroscopic methods used to characterize their optical and spin properties. In addition, preliminary simulation results of the spectral hole burning spectrum are presented, which are used to extract the hyperfine structure. Subsequently, five Eu^{3+} -based molecular systems are introduced, along with the corresponding experimental results. Two of these systems have already been published, while two further publications are currently in preparation for the remaining three. One of these molecular compounds, namely $[\text{Eu}(\text{BA})_4(\text{pip})]$, whose results were published by our collaborators within KIT and the REI community, served as a reference sample throughout this work. The detailed and

stepwise investigation of this molecular sample allowed us to develop and optimize our spectroscopy techniques and finally demonstrate coherent nuclear control, marking a significant milestone toward the full characterization of the material system.

The following experimental results were achieved through close collaboration and built upon previous Master's theses and ongoing doctoral work within our research group, particularly in collaboration with **Vishnu Unni C.**.

4.1. Excitation processes and phonon-assisted dephasing mechanisms in molecular materials

In ensemble spectroscopy, the REI ensemble is excited resonantly, exhibiting sharp spectral lines and long excited state lifetimes. Due to the parity-forbidden character of the $4f \rightarrow 4f$ transitions, direct excitation is inefficient in molecular systems, as the absorption cross section of the ion compared to the molecular backbone is relatively low. In order to improve luminescence efficiencies in molecular systems, the ligand environment is specifically designed to enhance sensitization mechanisms that enable the indirect excitation of the lanthanide ion via the local ligands, also known as the *antenna effect*. In the following, we briefly describe the mechanisms arising in REI-based molecular compounds. It should be noted that we use direct excitation, which can also cause excitations in the surrounding ligand fields and thus contribute to non-radiative multiphonon relaxation processes [107].

Antenna effect: Upon indirect excitation, the organic antenna absorbs light into its singlet excited state ($S_0 \rightarrow S_1$) and undergoes intersystem crossing to a lower-lying triplet state (T_1). Energy transfer then occurs from the triplet state to a favorable excited state of the lanthanide ion (e.g., 5D_0 in Eu^{3+} ions), typically via so-called *Förster* or *Dexter mechanisms*, which involve a non-radiative energy exchange at short distances on the order of 1 nm. This results finally in a $4f \rightarrow 4f$ transition from the lanthanide ion. Figure 4.1 schematically outlines the different mechanisms of a sensitization cycle arising in a molecular system. For chemical engineering, understanding the underlying processes within the molecular structure is crucial to prevent detrimental effects that adversely affect the luminescence efficiency [107].

Non-radiative MR processes and quantum yield: The most critical challenge in the design of REI-based molecular compounds is the minimization of nonradioactive deactivation pathways. One dominant quenching mechanisms includes MR, in which the excitation energy is transferred to high-energy, anharmonic vibrational modes within the ligand field. This typically involves X-H (X = C, O, and N) stretching modes with fundamental vibration frequencies around 3000 cm^{-1} . MR is especially pronounced in

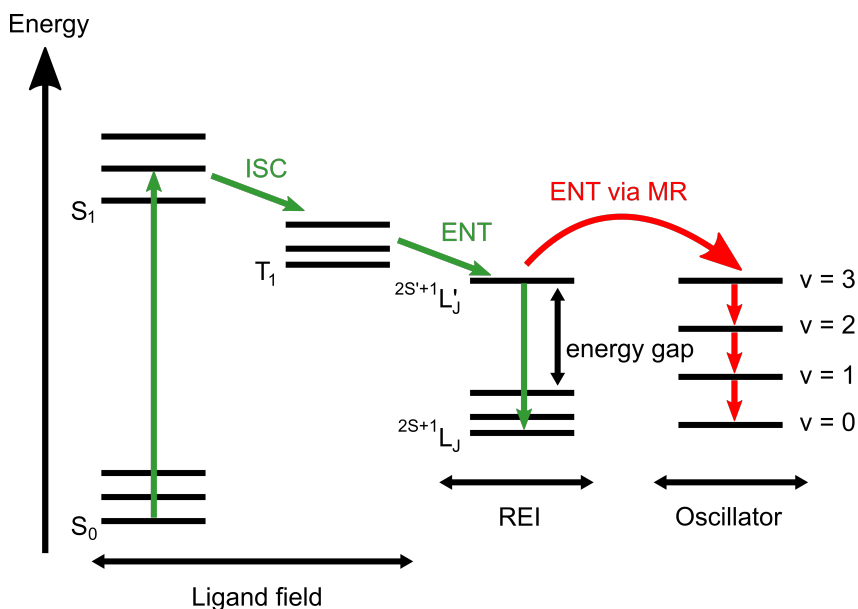


Figure 4.1: Schematic representation of typical energy transfer mechanisms within a REI-based molecular system. Due to the *antenna* effect, the organic ligand absorbs light and is excited from its singlet ground state (S_0) to the first excited singlet state (S_1), followed by intersystem crossing (ISC) to the triplet state T_1 . From there, energy transfer (ENT) occurs to the excited state of the lanthanide ion. The REI can then either emit light via radiative decay back to the ground multiplet, or undergo non-radiative multiphonon relaxation (MR) through coupling to vibrational modes (v denotes the vibrational quantum number). Figure is adapted from [107].

molecular systems due to the inherent structural flexibility of the molecular crystal lattice and weak Van-der-Waals interactions between the molecules, which result in diminished rigidity compared to inorganic crystalline solid-state hosts. As a consequence, the excited-state lifetime $T_{1,o}$ is reduced, lowering the intrinsic photoluminescence quantum yield of the respective REI, which is described by the relation [108]:

$$\phi_{\text{REI}} = \frac{T_{1,o}}{\tau_{\text{rad}}}, \quad (4.1.1)$$

where τ_{rad} denotes the radiative decay time. The intrinsic quantum yield thus serves as a figure of merit for describing the degree of non-radiative losses within the examined molecular system.

The efficiency of MR is governed by the energy gap ΔE between the emitting state and the next lower-lying electronic state: the smaller this gap, the more likely the excitation

energy will be quenched through MR processes. The corresponding non-radiative decay rate k_{nr} can be modeled by the *energy gap law* [107], which is expressed as:

$$k_{nr} = C_1 \cdot \exp\left(-C_2 \cdot \frac{\Delta E}{\hbar\omega_M}\right), \quad (4.1.2)$$

with C_1 and C_2 as empirical constants specific to a particular system, and $\hbar\omega_M$ as the energy of the deactivating vibrational mode. While the energy gap law model is most accurate when $\Delta E \gg \hbar\omega_M$ is fulfilled, it is commonly used as a crude approximation in REI-based systems, particularly in molecular complexes. For a more detailed description of this mathematical model, Ref. [107] can be reviewed.

Depending on the energy gap ΔE , the lanthanides are often classified into the following three categories with respect to their susceptibility to MR pathways [107]:

1. **Robust emitters with large energy gaps:** ΔE is on the order of $> 12\,000\text{ cm}^{-1}$. This group includes Eu³⁺ and Tb³⁺, which are relatively resistant to MR and can achieve high quantum yields.
2. **Moderately sensitive emitters with intermediate gaps:** ΔE ranges between 6800 and $12\,000\text{ cm}^{-1}$. This group includes Pr³⁺, Sm³⁺, Dy³⁺ and Yb³⁺. All are more susceptible to MR processes, which results in lower quantum yields. Their performance is usually increased by reducing the number of local high-energy oscillators in the direct vicinity of the ion.
3. **Highly susceptible near-infrared emitters with small gaps:** ΔE is on the order of $< 6800\text{ cm}^{-1}$. This group involves Nd³⁺, Er³⁺ and Tm³⁺. Due to their small energy gap, they exhibit strong MR and low quantum yields. Only specifically designed molecular environments can decrease the MR contribution.

Strategies for the reduction of MR pathways: Two primary approaches are used to reduce the contribution of MR in molecular systems:

1. *Deuteration*, where X–H bonds are replaced with X–D to lower the energy of the deactivating vibrational mode $\hbar\omega_M$.
2. *Perhalogenation*, particularly fluorination or chlorination, which replaces high-energy oscillators with lower-frequency counterparts, reducing the probability of MR processes. While perhalogenation offers stronger suppression of MR, it is limited to specific ligand systems due to chemical stability. In contrast, deuteration is widely applicable and preserves the general ligand structure.

In the specific case of Eu³⁺, where the $^5D_0 \rightarrow ^7F_6$ energy gap is around $12\,400\text{ cm}^{-1}$, MR can still occur in the proximal presence of high-energy oscillators, but with significantly lower probability. In addition to vibrational coupling, the symmetry of the ligand field influences the optical properties. Low-symmetry environments can increase the radiative decay rate, thereby reducing $T_{1,0}$ and thus increasing the optical transition probability of

the coherent transition. In conclusion, in order to realize promising REI-based molecular systems, chemical engineering must take into account both vibrational and symmetry degrees of freedom [37, 107].

4.2. Experimental methods

In this section, we will present the experimental techniques used to obtain the material properties of Eu^{3+} ions hosted in molecular compounds. Addressing and readout of the qubit states were carried out optically, while spin manipulation required an additional alternating current magnetic field, induced through a cylindrical RF coil. Regarding material properties, we distinguish between optical as well as spin properties and the primary focus is on the measurements that probe the intrinsic coherence of the emitter system in the presence of all dephasing mechanisms.

4.2.1. Optical properties

In order to investigate the fundamental optical properties of REI-based molecular systems, a specific set of spectroscopic techniques is employed. These include photoluminescence (PL) spectroscopy, spectral hole burning (SHB), free-induction decay (FID), and photon echo measurements. Each of these methods provides access to different optical parameters such as homogeneous linewidth Γ_h , excited-state lifetimes $T_{1,o}$, and optical dephasing and coherence times $T_{2,o}^*$ and $T_{2,o}$, respectively.

PL spectroscopy is typically used as an initial method to evaluate the emission properties and observe the number of sharp spectral lines arising from the $4f \rightarrow 4f$ transitions of the respective REI. Combined with pulsed off-resonant excitation, excited-state lifetimes $T_{1,o}$ can be obtained. SHB, in contrast, allows for probing of the homogeneous linewidth Γ_h by addressing specific subensembles of ions within the inhomogeneous distribution. Additionally, the detailed analysis of a whole SHB spectrum enables the extraction of the hyperfine structure of the corresponding isotope of the REI. We will show some first results in simulating and fitting the hole spectrum. FID and photon echo techniques are employed to study pure optical dephasing mechanisms and quantify coherence times $T_{2,o}$ ranging from nanoseconds to microseconds for REI-based molecular systems at the time [35]. This subsection summarizes the details of each spectroscopic method and gives some insights into analytical methods for SHB measurements.

4.2.1.1. Photoluminescence spectra

To obtain a PL spectrum, two approaches can be applied. At room temperature, we typically utilize off-resonant excitation using 532 nm light, which is near-resonant with

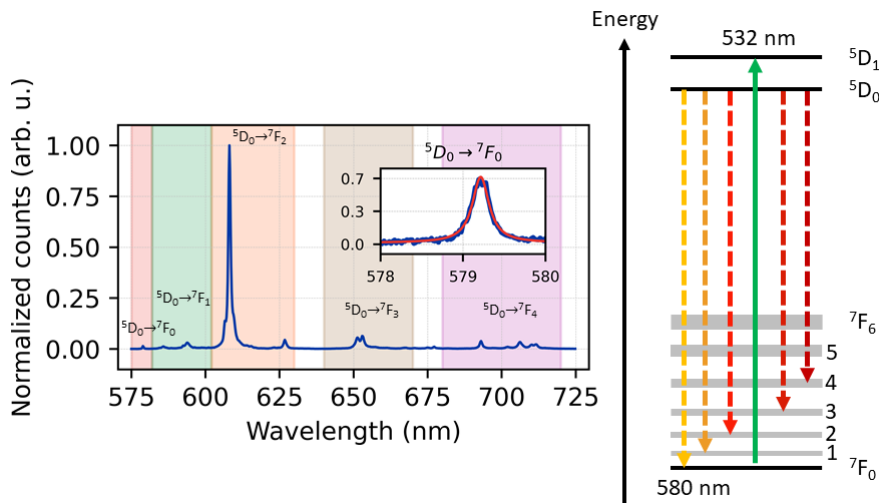


Figure 4.2: PL spectrum of an exemplary molecular complex. Example PL spectrum showing the emission from the $^5\text{D}_0$ state to the $^7\text{F}_j$ manifold with $J = 0$ to $J = 4$, which are indicated by the shaded regions. The inset displays the fitted $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. The corresponding electronic transitions are illustrated schematically alongside the spectrum, indicating the radiative decay channels from the $^5\text{D}_0$ excited state to the lower-lying $^7\text{F}_j$ ground state levels. The green arrow denotes the off-resonant excitation at a wavelength of 532 nm. The figure is adapted from [1].

the $^7\text{F}_0 \rightarrow ^5\text{D}_1$ and $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transition [109]. After excitation, the ions undergo non-radiative relaxation to the $^5\text{D}_0$ state, followed by radiative decay to lower-lying $^7\text{F}_j$ ground state levels, as schematically shown in Figure 4.2. The resulting spectral lines within the PL spectrum can be assigned to individual transitions to the $^7\text{F}_j$ levels. Figure 4.2 illustrates an exemplary room-temperature spectrum, showing the characteristic transitions up to $^7\text{F}_4$, while $^7\text{F}_5$ and $^7\text{F}_6$ occur at wavelengths around 750 nm and 820 nm, respectively. The excitation light is filtered out using a 532 nm notch filter.

Upon cooling to cryogenic temperatures, the individual transition frequencies experience a shift, so that the most efficient way includes off-resonant excitation of the REI ensemble with UV light to obtain the full spectrum. Otherwise, resonant excitation with ~ 580 nm can be performed, which results in the direct radiative decay from the $^5\text{D}_0$ state to the $^7\text{F}_j$ levels. However, the resulting spectrum will not include the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, as it is suppressed due to filtering of the excitation light by using a longpass filter (cutoff wavelength 597 nm).

Additionally, the optical lifetime $T_{1,0}$ can be measured by pulsed off-resonant excitation of the molecular sample with 532 nm light. The emitted fluorescence primarily arises from the dominating $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. After detection of the fluorescence signal,

the decay can be fitted with an exponential function in order to extract the excited-state lifetime $T_{1,0}$.

4.2.1.2. Spectral hole burning: measurement procedure and simulation

The occurrence of the inhomogeneous distribution of the REI ensemble was already discussed in Chapter 2. In order to gain insights into the homogeneous linewidth within the inhomogeneously broadened profile, SHB offers a straightforward and effective initial approach. In this method, a narrowband laser resonantly *burns* a hole into the inhomogeneous absorption profile by selectively exciting a class (typically not a single class) or subclass of ions. These ions are *optically pumped* from one ground-state hyperfine level and redistributed across the other levels. If the absorption profile is probed again after burning, with the frequency scanned over a defined range, a narrow spectral hole appears in the spectrum. The upper part of Figure 4.3 depicts the population dynamics occurring during the individual steps. The FWHM of the spectral hole, denoted as Γ_{hole} , is related to the homogeneous linewidth Γ_h by the following expression:

$$\Gamma_{\text{hole}} = 2 \cdot \Gamma_h. \quad (4.2.1)$$

The width of the spectral hole is twice the homogeneous linewidth because it reflects both the excitation profile and the intrinsic linewidth of the transition, which can be mathematically described as the convolution of two Lorentzian functions. When a narrowband laser excites a subclass of ions within the inhomogeneous profile, both the burn process and the subsequent probing contribute equally to the measured linewidth, resulting in a spectral hole width of twice the homogeneous linewidth.

If a wider frequency range is scanned, additional spectral features, including anti-holes and side holes, can appear due to population redistribution into other hyperfine levels. These features are observed as decreased or increased absorption holes and peaks at different frequencies, respectively. Because other ion classes experience slightly shifted transition frequencies and thus also hyperfine splittings, additional anti-holes and side holes may be observed upon probing the region around the burned hole. The details of the locations and strengths of the individual peaks are discussed in the simulation part.

In our experiments, we use a narrow-linewidth dye laser tuned near the center of the $^5D_0 \rightarrow ^7F_0$ (~ 580 nm) transition. The spectral hole can be measured either in absorption by collecting the transmission signal, which is filtered by a 580 nm bandpass filter, or in fluorescence by detecting the dominant emission of the $^5D_0 \rightarrow ^7F_2$ transition. The excitation light is removed using a 597 nm longpass filter.

The lower part of Figure 4.3 schematically illustrates our employed pulse sequence. The amplitude and frequency modulation is achieved by using the AOM in double-pass configuration. A first burn pulse excites and pumps the ions, followed by a probe pulse,

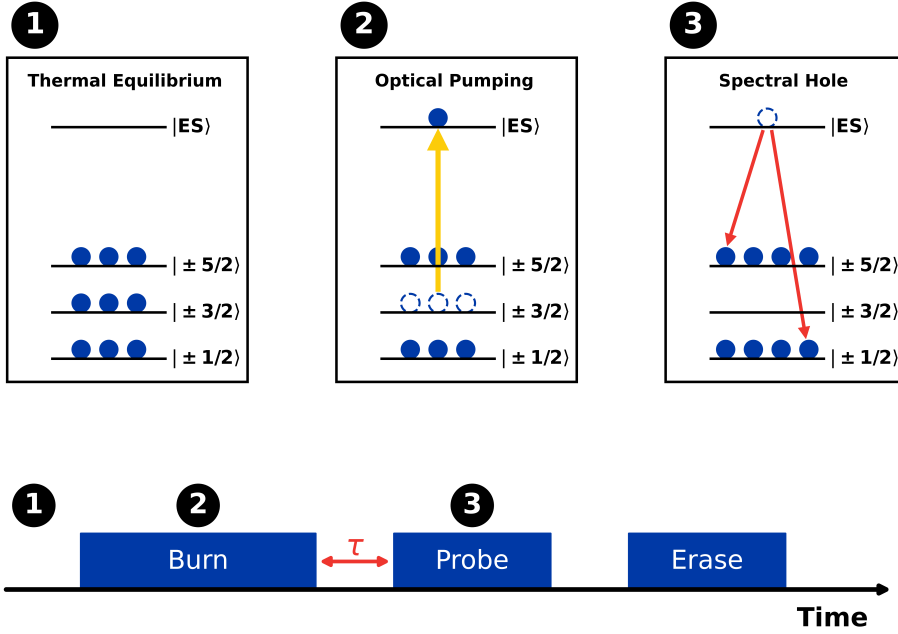


Figure 4.3: Population dynamics and pulse sequence of SHB. The upper panel depicts the evolution of the population distribution across the hyperfine levels. The population is initially distributed equally within the ground states. By applying a burn pulse to a specific hyperfine level, the respective population is optically pumped away and redistributed to other hyperfine states. A probe pulse, delayed by a time τ , reveals a narrow spectral hole in the absorption profile. The lower panel shows the corresponding pulse sequence used for a single SHB measurement. The numbers (black dots) denote the individual steps of the population dynamics during the applied sequence.

which scans a frequency window ranging from 20 up to 160 MHz (depending on the AOM capabilities), to resolve the burned spectral hole. In order to avoid power broadening or thermal effects, single shot measurements can be performed. Otherwise, for improving the signal quality, a defined number of SHB measurements can be repeated and averaged. Between each measurement, a small pause is included to enable thermalization of the sample. Finally, an erasing sequence concludes a single repetition, consisting of several short pulses scanned over a wide frequency range. This sequence serves to restore the population distribution to an equilibrium state, ensuring reproducible conditions for the subsequent measurement [46]. An overview of the employed pulse parameters can be found in Appendix A. Generally, each SHB measurement required a background reference in which no burn pulse was applied, specifically to remove the transient effects introduced by the AOM. The depth of these background-corrected spectral holes was then used for fitting.

First steps into the SHB simulation: In order to simulate and quantitatively reproduce SHB spectra, we use a simplified model based on the approach presented by Klieber *et al.* [110]. An additional overview of all involved transitions and population dynamics, which describes the exact occurrence of all spectral features during the SHB process can be found in Macfarlane *et al.* [50]. The model from Klieber captures the essential population dynamics among three hyperfine ground states and a single optically excited state. By solving the corresponding rate equations, the hole spectrum can be computed for the relevant pump and probe configurations. This simulation was complemented with an automated peak search algorithm, which searches for anti-hole features according to a defined transition matrix in order to extract the hyperfine splittings of the ground and excited states when real experimental data is provided.

The optical transition matrix element μ_{ge} between the ground state $\langle g \rangle$ and the excited state $\langle e \rangle$ can be separated into an electronic part, which is common to all optical transitions, and the overlap integral of the nuclear wavefunctions $|\xi\rangle$:

$$\mu_{ge} = \langle g | \mu E | e \rangle = \langle \psi_g | \mu E | \psi_e \rangle \langle \chi_g | \chi_e \rangle = \mu_o \langle \chi_g | \chi_e \rangle, \quad (4.2.2)$$

where $|\psi\rangle$ denotes the electronic component of the total wavefunction and $\langle \chi_g | \chi_e \rangle$ the overlap integral of the nuclear wavefunctions [110].

To model a first SHB spectrum, we consider a generic four-level system: three nuclear spin sublevels in the electronic ground state and one electronic excited-state sublevel. The burn laser pulse selectively drives the transition from $|1\rangle$ to $|4\rangle$. Transitions between excited-state hyperfine levels are neglected due to short electronic excited-state lifetimes relative to the hyperfine relaxation processes (also no transfer to other excited or CF levels is included). The time evolution of the state populations is governed by the following rate equations [110]:

$$\frac{d}{dt} \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{44} \end{pmatrix} = 2|\langle \chi_1 | \chi_4 \rangle|^2 \left(\frac{\mu_o E}{2\hbar} \right)^2 T_2 \begin{pmatrix} -1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{44} \end{pmatrix} + \begin{pmatrix} -(\Gamma_{12} + \Gamma_{13}) & \Gamma_{12} & \Gamma_{13} & \Gamma_{41} \\ \Gamma_{12} & -(\Gamma_{12} + \Gamma_{23}) & 0 & \Gamma_{42} \\ \Gamma_{13} & \Gamma_{23} & -(\Gamma_{13} + \Gamma_{23}) & \Gamma_{43} \\ 0 & 0 & 0 & -1/T_1 \end{pmatrix} \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{44} \end{pmatrix}. \quad (4.2.3)$$

The first term describes optical pumping between the states $|1\rangle$ and $|4\rangle$, driven by the laser field, as illustrated in Figure 4.4. The rate is proportional to the square of the optical Rabi frequency Ω_R and scaled by the optical coherence time T_2 , assuming only resonant excitation. The second term models the relaxation processes: the upper left 3×3 block accounts for the hyperfine relaxation among the ground-state sublevels (with $\Gamma_{ij} = \Gamma_{ji}$

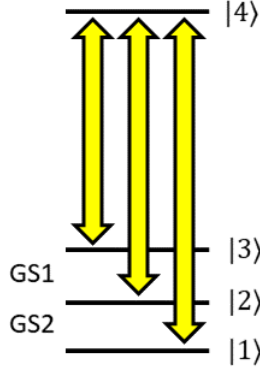


Figure 4.4: Pump model used for the SHB simulation. The model includes three hyperfine ground states and one excited-state sublevel, with transitions described by rate equations that capture the population transfer and the relaxation process, while neglecting coherent effects, and population exchange to other excited or CF states.

for $i = 1, 2, 3$ under the high-temperature approximation), while the final row describes the spontaneous decay from the excited state.

The optical decay rates Γ_{4i} are determined by the nuclear wavefunction overlap [110], which includes the oscillator strengths of the individual transitions:

$$\Gamma_{4,g(g=1-3)} = \frac{|\langle \chi_4 | \chi_g \rangle|^2}{T_1}. \quad (4.2.4)$$

A probe pulse scanned in frequency detects changes in absorption when the resonance condition is fulfilled, for instance, when the probe is resonant with a transition influenced by the population redistribution caused by the burn pulse. As a consequence, the change in the absorption signal is described by [110]:

$$\Delta A(\Delta\omega) = |\langle \chi'_e | \chi'_g \rangle|^2 (\rho_{g'g'} - \frac{1}{3}) L(\Delta\omega). \quad (4.2.5)$$

with $|g'\rangle$ and $|e'\rangle$ denoting the ground and excited states coupled by the probe laser field, and $L(\Delta\omega)$ denotes a Lorentzian line shape centered around the resonance frequency ω_0 . The factor $\rho_{g'g'} - \frac{1}{3}$ represents the deviation from thermal equilibrium. In order to obtain the full SHB spectrum, the equilibrium populations $\rho_{g'g'}$ are calculated for each of the nine possible pump transitions ($g, e = 1, 2, 3$). For each pump configuration, the probe laser field can address nine possible transitions, leading to a total of 81 transitions, as shown in Figure 4.5. Accounting for degeneracies, the resulting spectrum contains 49 distinguishable resonance lines, including the central hole, side holes, and anti-holes [110, 50].

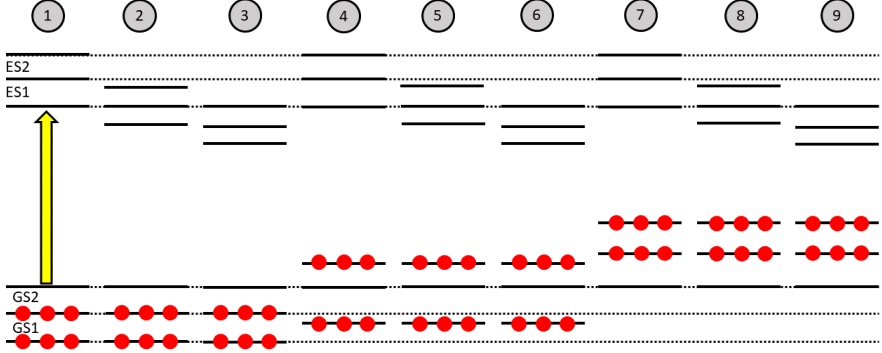


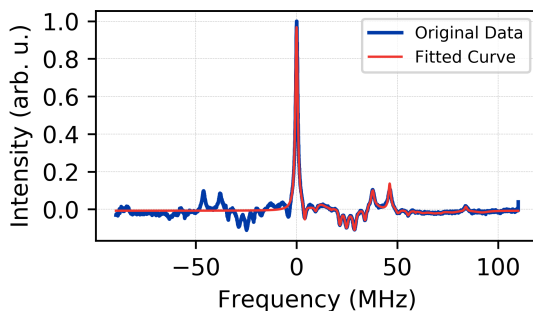
Figure 4.5: Overview of the nine pump configurations used in the SHB model. Each configuration corresponds to optical pumping from one of the three ground-state sublevels to one of the three excited-state sublevels. The population redistribution resulting from all individual pump configurations determines the absorption change observed during probing and contributes to the full spectral hole pattern. Picture is adapted from [98].

From the nine possible pump configurations, a transition matrix can be constructed for each case, containing the relevant hyperfine splittings between the ground-state and excited-state sublevels. Accordingly, the knowledge of the matrix for one pump configuration is sufficient to generate the complete set of nine configurations by appropriate index permutations. The respective entry of the transition matrix and the oscillator strength of the corresponding transition (which determine the relative transition amplitudes) are then plugged into Equation 4.2.5. With this procedure, each individual feature can be determined. A precise simulation of a specific material system can only be performed, when all parameters including oscillator strengths and hyperfine splittings are obtained from measurements. This enables direct comparison with experimental data and allows for quantitative extraction of such parameters. The transition matrix for one pump configuration is defined as follows:

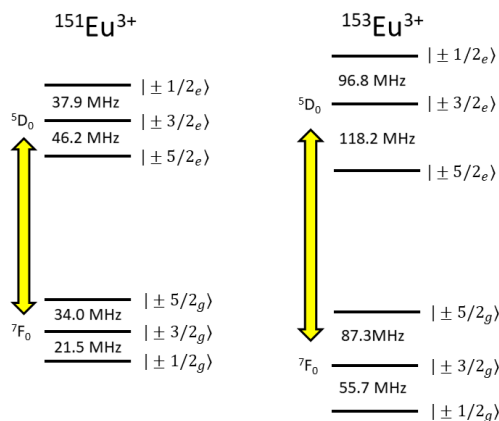
$$\begin{pmatrix} O & ES1 & ES1 + ES2 \\ -GS1 & -GS + ES1 & -GS1 + ES1 + ES2 \\ -GS1 - GS2 & -GS1 - GS2 + ES1 & -GS1 - GS2 + ES1 + ES2 \end{pmatrix}, \quad (4.2.6)$$

where $GS1$ and $GS2$ denote the ground-state hyperfine splittings, and $ES1$ and $ES2$ refer to the excited-state hyperfine splittings. This transition matrix corresponds to the seventh pump configuration illustrated in Figure 4.5, where the burn laser is resonant with the transition from the highest ground state level to the first excited-state level.

To simulate the spectral hole pattern, we use the available data reported in the publication by our collaborators [1]. Based on these values, we implemented a peak search algorithm that identifies the positions of anti-holes and side holes in the measured absorption spectrum. The detected spectral features are then compared to the expected resonance



(a)



(b)

Figure 4.6: Fitting of the reference SHB data and the corresponding hyperfine splittings of the molecular complex $[\text{Eu}(\text{BA})_4(\text{pip})]$. (a) Fitted spectral hole pattern (red curve) on the right wing of the central hole compared with the measured data (blue), obtained from isotopically purified molecular samples of the $^{151}\text{Eu}^{3+}$ isotope. The data are taken from [1]. (b) Reported hyperfine splittings for the two isotopes of the molecular complex $[\text{Eu}(\text{BA})_4(\text{pip})]$. The figure is adapted from [1].

positions calculated from the transition matrix. If the experimental data contains no overlapping contributions from other isotopes and offers sufficient resolution of the weaker side features, the probability of accurately extracting the correct hyperfine splittings increases significantly. At this stage, the model does not include the extraction of oscillator strengths. Figure 4.6(a) presents the resulting fit based on the published data for the $^{151}\text{Eu}^{3+}$ isotope, successfully revealing the hyperfine splittings in both the ground- and excited-state levels. In the simulation, only the right side of the data was fitted, primarily due to better-resolved peaks and slight asymmetry in the spectrum.

For comparison, the previously reported hyperfine splittings for both isotopes of the molecular complex $[\text{Eu}(\text{BA})_4(\text{pip})]$ are illustrated in Figure 4.6(b) [1].

4.2.1.3. Optical free-induction decay

An optical FID is the coherent emission from a subensemble of ions excited by a narrow-band laser pulse of a bandwidth $\Delta\nu$ and pulse duration Δt . The laser pulse addresses only a narrow spectral fraction of the ensemble within the inhomogeneous line, preparing a coherent optical superposition among the resonant ions. This sequence is schematically shown in Figure 4.7(a), where a single excitation pulse acts as a $\pi/2$ pulse, rotating the Bloch vector into the equatorial plane and initiating the FID signal. The subsequent decay of coherence begins immediately after this excitation pulse and continues until the readout pulse is applied. The evolution of this coherence is visualized in Figure 4.7(b), which shows a sequence of three Bloch spheres: the initial superposition after the $\pi/2$ pulse, partial dephasing at an intermediate time, and complete dephasing at the end of the FID evolution. Over time, the coherence decays due to homogeneous dephasing mechanisms such as interactions with the environment, fluctuations, and phonon-induced processes, leading to an exponentially decaying FID signal.

To detect this weak emission, we apply a heterodyne detection scheme: a frequency-shifted probe pulse overlaps with the FID emission, producing a beat signal from which the FID amplitude can be extracted. In the weak excitation regime ($\Omega^2 \cdot T_1 \ll 1/T_2$), the amplitude of the heterodyne signal decays exponentially with $T_2/2$, neglecting instrumental limitations (frequency jitter of the laser) or power broadening effects [49]. The extracted decay constant constitutes the pure dephasing time $T_{2,o}^*$. Under experimental conditions, our readout pulses are positioned directly after the excitation pulse, with almost no delay time, as the FID decay occurs on short time scales on the order of a few hundred nanoseconds.

4.2.1.4. Photon echo

In order to measure the optical coherence time T_2 , the two-pulse photon echo technique can be employed. Figure 4.8(a) represents the pulse sequence. A first $\pi/2$ laser pulse creates a coherent superposition between the states of the optical transition of the ion ensemble, rotating the Bloch vectors into the equatorial plane of the Bloch sphere, as shown in Figure 4.8(b). This pulse is resonant within a frequency range $\Delta\nu$ around a central frequency ω_0 . Due to inhomogeneous broadening and local interactions with the environment, ions that are detuned from ω_0 begin to precess at different rates, leading to dephasing of the ensemble and thus a decay of the macroscopic polarization, which corresponds to the previously discussed FID. In the Bloch sphere visualization, the vectors fan out over time as they rotate at slightly different frequencies. After a delay time τ , a π pulse is applied, inverting the phase evolution, which causes the

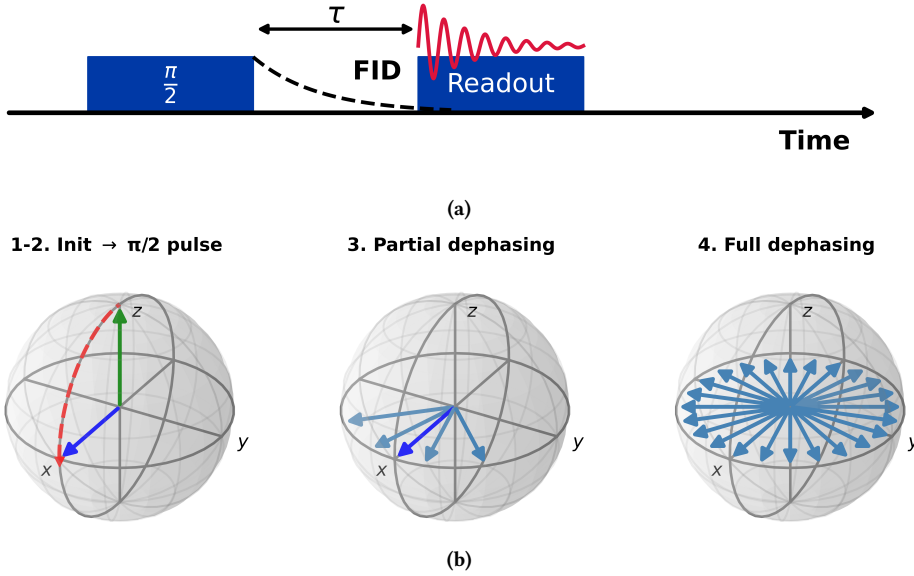


Figure 4.7: Pulse sequence and Bloch vector visualization of the FID. (a) The upper panel represents the pulse sequence for the optical FID and heterodyne detection. A weak excitation pulse prepares the optical coherence, while a delayed and detuned readout detects the beating signal from the emitted FID, which is illustrated as an exponential decay (dashed black line) after the $\pi/2$ pulse. (b) The lower panel illustrates the Bloch sphere representation of the FID process. A $\pi/2$ pulse rotates the ensemble Bloch vector into the equatorial plane, creating a coherent superposition. After the pulse, individual Bloch vectors from spectrally distinct subgroups begin to dephase at different rates and directions, depending on their detunings within the inhomogeneous line. This dephasing causes the ensemble Bloch vector to decay exponentially, resulting in the observed FID signal.

Bloch vectors to refocus and after another delay time τ , they rephase, corresponding to in-phase oscillations. This results in a renewed macroscopic polarization of the ion ensemble and thus the emission of a photon echo [46].

Experimentally, the emitted signal is very weak, so a heterodyne detection scheme is used, as in the case of the FID. The photon echo interferes with a reference field, which is frequency-detuned, generating a beat signal. For each value of the delay time τ , a Fourier transform of the measured beating yields the echo amplitude. By recording the echo amplitude as a function of the total delay time, the decay of the photon echo can be obtained. The Fourier-transformed beating signals are fitted with Gaussian functions

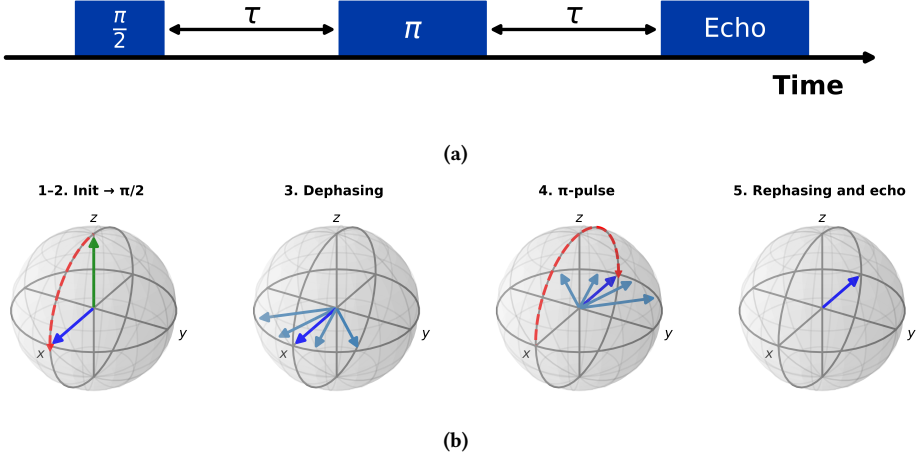


Figure 4.8: Pulse sequence and Bloch vector visualization of the photon echo. (a) Pulse sequence for the two-pulse photon echo experiment. A $\pi/2$ pulse prepares the optical coherence. After a first delay time τ , a π pulse inverts the phase evolution. The echo is emitted at a total time of 2τ , which is detected via a heterodyne readout pulse. (b) The lower panel illustrates the Bloch sphere representation. The $\pi/2$ pulse rotates the Bloch vector into the equator, followed by dephasing of the excited ion ensemble. The π pulse reverses the phase evolution, leading to a refocusing and thus an echo emission.

in order to extract the echo amplitude. The echo intensity $I_{\text{echo}}(\tau)$ decays exponentially with increasing delay time τ as follows [46]:

$$I_{\text{echo}}(\tau) = \exp\left(-\frac{4\tau}{T_2}\right), \quad (4.2.7)$$

providing direct insight into the optical coherence time T_2 . The pulse durations need to be much shorter than the optical dephasing time $T_{2,0}^*$, otherwise no coherence can be created. In our case, we probe samples with a Eu^{3+} doping concentration of 100 %, resulting in a large ensemble. Although the same pulse duration is used for both the $\pi/2$ and π pulses, the inhomogeneous distribution of Rabi frequencies ensures that a subset of the ensemble still undergoes approximately the intended rotation.

4.2.2. Spin properties

REI-based materials are primarily known for their exceptionally long hyperfine coherence times, making them promising for quantum information applications, particularly quantum memories. While optical transitions typically allow for coherence times up to the millisecond range, hyperfine transitions can exhibit intrinsic coherence times of several seconds or more. The current record for the nuclear spin coherence time $T_{2,s}$ is about 18 h, achieved in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ using a combination of the ZEFOZ technique and dynamical decoupling [21]. Even longer timescales have been observed for hyperfine lifetimes in the same material, reaching up to 49 d [67, 111].

Given the promising optical properties and long hyperfine lifetimes recently reported in Eu^{3+} -based molecular complexes [1, 37], the next logical step involves not only designing and synthesizing new molecules but also demonstrating coherent nuclear control. This subsection outlines the spectroscopic techniques used to investigate the spin properties of our reference molecular complex. Specifically, we focus on measurements that characterize the hyperfine lifetimes $T_{1,s}$, spin inhomogeneous linewidths $\Gamma_{\text{inh},s}$ via optically detected nuclear magnetic resonance (ODNMR), and spin coherence times $T_{2,s}$. The latter are determined through spin echo and Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences, which enable coherent control and dynamical decoupling from local environmental fluctuations.

4.2.2.1. Hyperfine lifetime measurement

In order to gain insight into the hyperfine spin level dynamics, a commonly used analysis method is to study the time dependence of spectral holes, where a series of SHB measurements is performed at different delay times τ between the burn and probe pulses, allowing the evolution of the hole depth to be tracked over time. The burn pulse depletes a hyperfine spin level, causing the fluorescence signal to decrease before reaching saturation, where a steady-state equilibrium is established between optical pumping-induced population redistribution and ground-state spin relaxation back into the burned state. For a single measurement, the probe pulse reveals a spectral hole, as described in the previous Subsection 4.2.1. With increasing delay time τ , more population returns to the hyperfine levels, leading to a gradual reduction in hole depth when probed. The pulse sequence used in the experiments and the corresponding population dynamics are schematically depicted in Figure 4.9. Above the pulse sequence, the population dynamics are shown for the corresponding points in time throughout the sequence. As the hole depth decreases over time, this reduction follows an exponential decay, revealing the hyperfine lifetime $T_{1,s}$, which defines the upper limit of the delay time. The optical lifetime $T_{1,o}$ sets the lower limit, determining the earliest time at which a spectral hole can be observed.

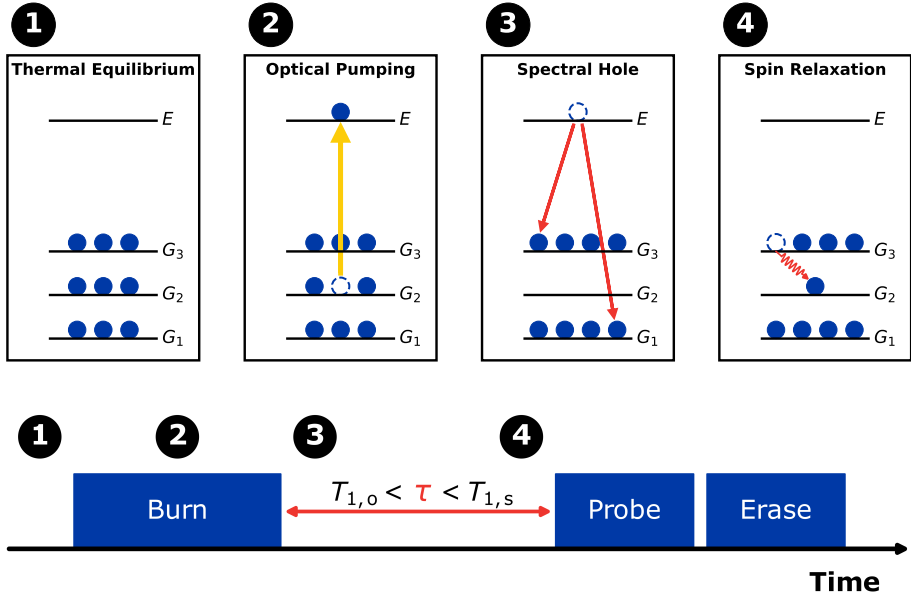


Figure 4.9: Hyperfine lifetime measurement. Schematic illustration of the spin level dynamics and the SHB pulse sequence used to determine the hyperfine lifetime $T_{1,s}$. By varying the delay time τ (highlighted in red) between the burn and probe pulses, the decay of the spectral hole depth can be observed, which reveals the hyperfine spin state lifetime. This lifetime defines the upper limit for the delay time, while the optical lifetime $T_{1,o}$ sets the lower limit. The level structures shown above the pulse sequence represent the spin dynamics during individual steps. After the probe pulse, an erasing sequence can be applied to restore the hyperfine level population to an equilibrium-like state.

For the experiment, the decay of the spectral hole was typically measured over delay times ranging from 10 ms to approximately 20 min. The feasibility of achieving longer waiting times depends mainly on the properties of the investigated material system. However, laser instabilities can lead to significant spectral drifts, and if they become too large, the scanning window of the probe pulse may fail to detect the burned spectral hole. To ensure sufficient contrast and a good signal-to-noise ratio (SNR) even at long waiting times, the spectral holes were burned using relatively high optical power, sometimes up to several milliwatts, achieving at least 50 % contrast. Since power broadening was not a concern for this measurement technique, the use of high optical powers did not limit the results. Similar to standard SHB experiments, each measurement also required a background reference where no burn pulse was applied to exclude unwanted contributions. Most hyperfine lifetime measurements were conducted at liquid helium temperatures. With the arrival of our dilution refrigerator, we were able to examine

4. Ensemble spectroscopy of Eu^{3+} -based molecular complexes

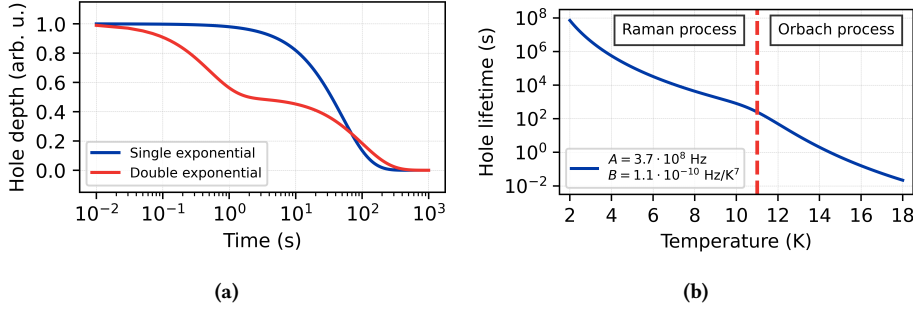


Figure 4.10: Temperature dependence of the spin hole lifetime. (a) The hole depth exhibits exponential decay over time, which is influenced by temperature and by different spin-lattice interaction strengths among the three ground state levels, potentially leading to multiple decay rates. Könz *et al.* [67] conducted a detailed study on the hyperfine lifetime of Eu^{3+} in Y_2SiO_5 across various temperatures to explore the primary relaxation mechanisms. (b) The resulting curve is modeled by the Equation (4.2.8), with fit coefficients A and B derived from their study for $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ at symmetry site 1. Below 12 K, inelastic Raman scattering predominates. Above this threshold, two-step Orbach processes become the dominant mechanism.

some materials at millikelvin temperatures, ranging from 50 mK to 500 mK. Detailed specifications of both measurement and pulse parameters are provided in Appendix A.

The observation of two distinct time constants in spectral hole decay measurements is often explained by the presence of multiple spin-lattice relaxation rates among the three ground-state hyperfine levels of each Eu^{3+} isotope (two naturally abundant isotopes of Eu^{3+}). As noted in Könz *et al.* [67], such multiexponential decays are expected and observed in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$. Temperature plays a crucial role in this process. At low temperatures, hyperfine lifetimes can reach up to several weeks (20 d at 2 K for site 1 in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ [67]), while at temperatures between 15 and 20 K, the hole lifetime drops drastically to about 1 s for both sites. However, ion concentrations have little impact on the hole lifetime.

The relaxation rates span multiple timescales: at low temperatures (< 4 K), the fast component is mostly observed. At higher temperatures (> 15 K), the slow component dominates. In the intermediate regime, both time constants can be detected, likely due to contributions from the site symmetry, isotope-specific behavior, or varying transition rates among the ground-state hyperfine levels. Preparing a single spin state could help to clarify which hyperfine levels contribute to the distinct relaxation components.

As already mentioned in Subsection 2.2.2 of Chapter 2, possible spin-lattice relaxation mechanisms include direct one-phonon processes, two-phonon Orbach processes, and

inelastic two-phonon Raman interactions. The hyperfine lifetime $T_{1,s}$ can be modeled from the individual phonon-mediated contributions [67]:

$$T_{1,s} = \left[\frac{A}{\exp(\Delta E/k_B T) - 1} + BT^7 \right]^{-1}, \quad (4.2.8)$$

where A and B denote the coefficients corresponding to the Orbach and Raman processes, respectively, and ΔE represents the energy difference between the 7F_0 and 7F_1 levels. At cryogenic temperatures below 12 K, the Raman process dominates, while at elevated temperatures, resonant two-phonon Orbach processes become increasingly significant due to higher phonon occupation [67].

4.2.2.2. Optically detected nuclear magnetic resonance

The ODNMR technique is a highly sensitive method for probing nuclear spin transitions in REI-based systems. In ensembles, this reflects the spin inhomogeneous broadening $\Gamma_{\text{inh},s}$. It works by optically preparing either a spectral hole or a spectral pit using the respective preparation method and detecting changes in the absorption or fluorescence signal as a function of the applied RF frequency. The respective population dynamics is illustrated in the upper panel of Figure 4.11. As originally demonstrated by Erickson *et al.* [112], RF excitation resonant with the ground-state hyperfine transitions can refill the optically burned hole, leading to an increase in fluorescence. The ground-state splittings are resolved directly by the RF resonance [50]. In our experiments, we employed different variations of this technique. The typical pulse sequence is depicted in the lower panel of Figure 4.11. The spin polarization can be performed using simple burn pulses or complex class preparation methods, where only a single or few classes are driven by the RF field. The central criterion is to prepare a large population difference between the hyperfine levels of the probed transition. This difference will determine the signal contrast of the resulting spin inhomogeneous line. The RF signal can be applied in discrete frequency steps or in a continuous-wave (CW) chirp. Both techniques collect the emitted fluorescence, which is then plotted over the RF frequency. The spin inhomogeneous lines are fitted with Lorentzian functions. Typical RF powers range from a few hundred milliwatts up to a maximum power of about 120 W. While ODNMR detects population differences, it can be extended with pulsed RF techniques to perform spin echoes in order to extract the spin coherence time $T_{2,s}$.

4.2.2.3. Spin echo and dynamical decoupling control

The intrinsic spin coherence time $T_{2,s}$, which is the figure of merit for most quantum technologies, can be accessed through refocusing techniques such as the spin echo which is similar to the photon echo but operates in a different frequency domain. The simplest method to mitigate pure dephasing processes is the *Hahn spin echo* sequence,

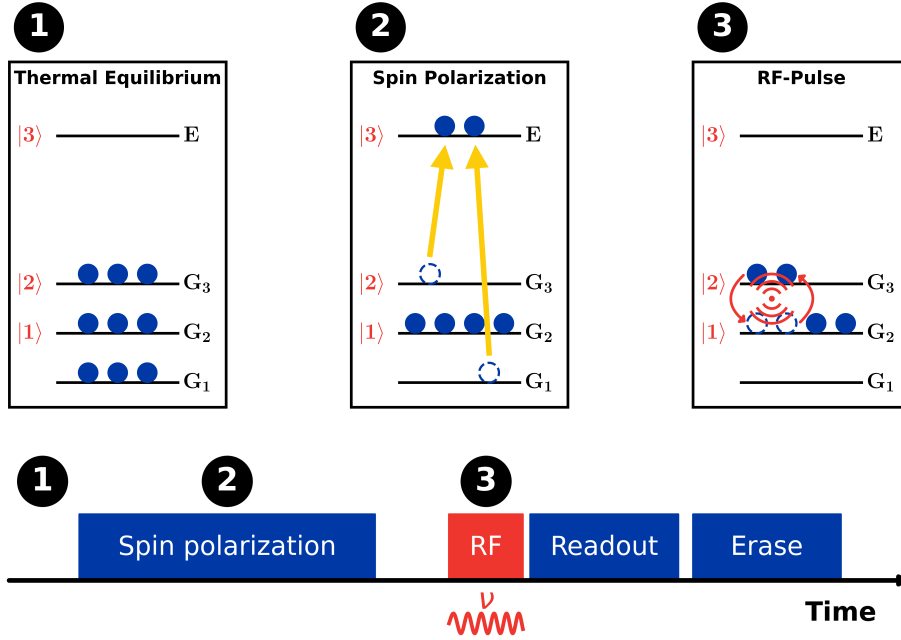


Figure 4.11: Optically detected nuclear magnetic resonance. Overview of the energy level structure and population dynamics during the pulse sequence used to determine the spin inhomogeneous linewidth. For clarity, the spin state polarization is represented as a bichromatic pulse following the Λ -scheme, marked in red ($|1\rangle$, $|2\rangle$ and $|3\rangle$). If a specific hyperfine level is initialized, an RF pulse resonant with the qubit transition transfers a fraction of the population to the other hyperfine state. The readout occurs immediately after the RF pulse, during which the fluorescence is detected, providing information about the population distribution. To probe the spin inhomogeneity, the frequency is either chirped over the hyperfine splitting (red sine) or the pulse sequence is repeated at multiple discrete frequencies, allowing a pointwise reconstruction of the hyperfine response. Finally, an erase pulse resets the population distribution, preparing the system for the next measurement cycle. Blue boxes denote optical pulses used for spin preparation and readout, while the red boxes represent the RF pulses.

where a $\pi/2$ pulse creates a superposition between two hyperfine states, followed by a π refocusing pulse after a delay time τ . This inverts the accumulated phase errors and produces a spin echo signal at the time 2τ [113]. In our measurement schemes, we rely on population detection via the fluorescence signal. For this reason, a final $\pi/2$ pulse is added to project the coherence into a detectable population, which is read out with an optical pulse. Figure 4.12(a) schematically shows the spin echo sequence used in our measurements. The spin preparation is achieved by preparing optical spectral pits.

However, a single refocusing pulse only corrects time-independent or static dephasing ($> \tau$). For environments with slowly fluctuating noise including spin baths, spin impu-

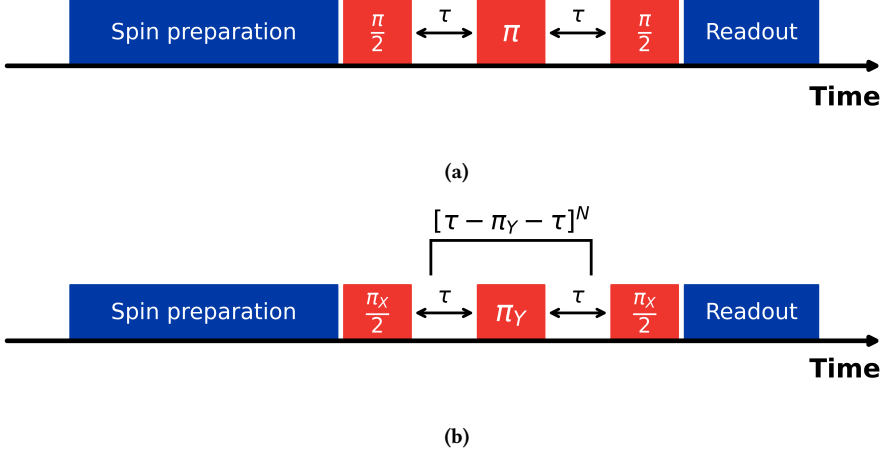


Figure 4.12: Spin echo and dynamical decoupling sequences. (a) The upper panel shows the standard spin echo sequence, where a $\pi/2$ pulse creates the superposition, followed by a π pulse after a delay time τ , leading to rephasing of the spins and the formation of an echo at the time 2τ . The echo amplitude is read out via the fluorescence signal reflecting the population. For this reason, a final $\pi/2$ pulse is applied to convert the coherence into a population. (b) The lower panel illustrates the CPMG echo sequence, where the initial $\pi_x/2$ pulse rotates the spins into the equatorial plane, and a series of N π_y pulses applied around a different axis, repeatedly refocus the dephasing spins. This sequence extends the effective spin coherence time $T_{2,s(\text{CPMG})}$ by maintaining rephasing at regular intervals. A final $\pi_x/2$ pulse is again used to project the remaining coherence onto a population for the detection. Blue boxes denote optical pulses used for spin preparation and readout, while the red boxes represent the RF pulses.

rities, or charge noise, a sequence of multiple equally spaced refocusing π pulses can further extend the coherence time, which is the simplest form of dynamical decoupling (*Carr–Purcell* (CP) sequence). However, the single pulses are imperfect (creating over- or under-rotations) and introduce phase errors, meaning that after a certain number of refocusing pulses, the coherence will be lost. In order to compensate for pulse imperfections, the *Carr–Purcell–Meiboom–Gill* (CPMG) sequence constitutes a reliable technique, which applies the refocusing π_y pulses around a different axis, in our case the y-axis. This ensures that pulse errors do not accumulate as strongly, especially for even-numbered pulses, and the echoes appear consistently all along the same axis [113]. Figure 4.12(b) depicts the CPMG sequence employed in our measurements. As in the standard spin echo experiment, the spin preparation and readout are performed optically. A final $\pi_x/2$ pulse, applied around the x-axis, converts the remaining coherence into a population for the optical detection. Typical RF powers used for the pulses range from 50 up to approximately 120 W.

The echo amplitudes in these sequences decay exponentially as a function of the total delay time 2τ (for CPMG: $N \cdot 2\tau$), with a time constant representing the intrinsic $T_{2,s}$. This holds under the condition that the pulse spacing is shorter than the correlation time of the environmental fluctuations, which can thereby be averaged out or canceled. Such dynamical decoupling sequences offer a powerful tool to probe and extend spin coherence times in quantum systems [113]. While more advanced and robust dynamical decoupling sequences, such as the *XY* set or *Knill* composite pulses, exist, in this work we only employed the CPMG scheme due to its simplicity and effectiveness.

4.3. Measurements on Eu^{3+} ensembles in molecular complexes

This section presents the spectroscopic characterization of various Eu^{3+} -based organic molecular complexes, constituting the central part of this thesis. The primary motivation behind investigating different molecules based on Eu^{3+} was to identify suitable candidates for quantum information applications according to their optical and spin properties. Since our experimental approach involves integration into an optical cavity to enhance light-matter interaction, sample preparation methods are also of great importance and need to be adjusted in comparison to our standard fiber-based ensemble spectroscopy. For this reason, every new sample is first screened for its general optical characteristics using the methods described in Section 4.2, and subsequently evaluated for its potential integration into our cavity setups. Special emphasis is placed on the main reference molecule $[\text{Eu}(\text{BA})_4(\text{pip})]$ [1], which has been shown to possess one of the longest optical coherence times reported among molecular Eu^{3+} systems and coherence properties comparable to those of some diluted and stoichiometric inorganic Eu^{3+} platforms [35, 114, 115]. One of the main goals of this thesis was to reproduce the reported optical properties and conduct preliminary investigations of its nuclear spin properties. However, since $[\text{Eu}(\text{BA})_4(\text{pip})]$ is not an ideal candidate, primarily due to the low branching ratio of its coherent transition, the search for an improved molecular system was necessary. All molecular complexes presented in this thesis were synthesized and provided by our collaborators in the group of **Professor Mario Ruben** at the Institute of Nanotechnology at KIT. Although not every investigated molecular compound proved suitable for use as a spin-photon interface, their characterization provided valuable insights into the effects of chemical modifications compared to previously studied samples.

4.3.1. Analysis of the molecular complex $[\text{Eu}(\text{BA})_4(\text{pip})]$

In this subsection, we focus on the detailed characterization of the reference molecule $[\text{Eu}(\text{BA})_4(\text{pip})]$, previously studied by our collaborators **Diana Serrano** and **Philippe**

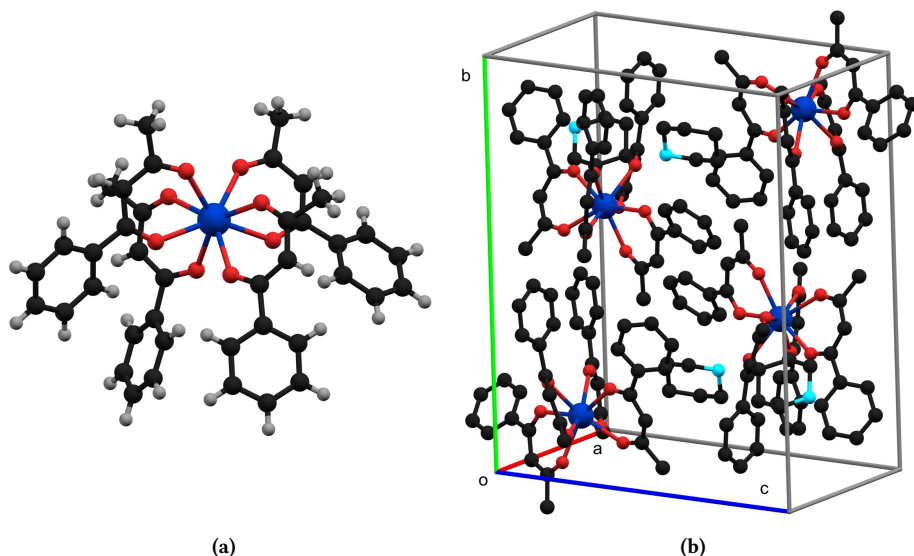


Figure 4.13: Crystal structure of $[\text{Eu}(\text{BA})_4(\text{pip})]$. (a) X-ray crystal structure of a single $[\text{Eu}(\text{BA})_4(\text{pip})]$ molecular complex. For better visualization, only the anionic part of the molecule is depicted. Europium is shown in blue, oxygen in red, carbon in black, and hydrogen in gray. (b) The unit cell involves four molecules with a different orientation in the monoclinic crystal structure. The counter cations of the molecular complexes are included, but the hydrogen atoms are omitted. Nitrogen is shown in cyan.

Goldner from Chimie ParisTech (France), as well as **Senthil Kumar Kuppasamy** from KIT [1]. For clarity, we refer to this molecular compound as **SKR520**. To verify and reproduce these published results, we initially characterized the optical properties of SKR520 in microcrystalline powder form both at room temperature and at cryogenic temperatures, followed by exploring alternative sample preparation methods for cavity integration, including spin coating and recrystallization. Moreover, we extended this investigation by introducing coherent control of the nuclear spin states, thereby addressing a major challenge in molecular systems to date and paving the way for their potential implementation in future quantum information applications. A publication detailing the results of the spin characterization of the reference sample SKR520 is currently in preparation [116].

The molecular structure of $[\text{Eu}(\text{BA})_4(\text{pip})]$ is illustrated in Figure 4.13(a), highlighting its mononuclear configuration, with the Eu^{3+} ion coordinated by four benzoylacetate (BA) ligands. These ligands form an anionic complex, balanced by cationic piperidin-1-ium (pip) units, which are omitted in this part for clarity. The all-oxygen coordination environment of the Eu^{3+} center can be described as a biaugmented trigonal prism and exhibits a C_{2v} point group symmetry [48]. Figure 4.13(b) shows the corresponding unit cell of the crystal lattice, which belongs to the monoclinic space group $P2_1/n$. From the

arrangement of the four molecular constituents within the unit cell, it can be seen that the individual orientations relative to one another are all different. With the structural and coordination properties of SKR520 established, we now turn to the synthesis process, which we have repeatedly and reliably used to produce the sample ourselves as well, followed by a detailed characterization and discussion of the experimental results.

4.3.1.1. Synthesis of $[\text{Eu}(\text{BA})_4(\text{pip})]$

The molecular material itself is a well-known solid-state laser medium that was already reported in the 1960s [115, 117]. The primary reason our collaborators selected this complex for investigation is its straightforward synthesis procedure via a one-pot reaction using commercially available reagents: 1-phenylbutane-1,3-dione, piperidine, and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ³⁵. The synthesis followed a modified procedure based on Melby *et al.* [118]. In a first step, the ligand material 1-phenylbutane-1,3-dione (1.3 g, 8 mmol) was dissolved in 20 mL of ethanol at 75 °C under stirring. After successful dissolution, piperidine (0.8 mL, 8 mmol) was added, and the solution was stirred for 15 min, during which it should turn pale yellow as the ligands undergo deprotonation. With the stirring period completed, an aqueous solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (32 mg, 2 mmol in 10 mL H_2O) was added to the reaction mixture, which was then stirred without heating at room temperature for at least 24 h. Finally, the process results in the formation of a half-white microcrystalline precipitate of the molecular complex. The precipitate was then filtered, washed several times with 50 mL of ethanol, and dried either in the fume hood of the chemistry lab or in a vacuum chamber under reduced pressure for a minimum of 12 h. Based on our experience, SKR520 is a chemically robust complex and can be stored under ambient conditions, with possible degradation occurring only after prolonged periods (≈ 1 year) or contamination with impurities.

Our collaborators prepared and investigated a series of different forms of SKR520, including a stoichiometric natural-abundance version, several Y^{3+} -diluted versions, and an isotopically purified version of the $^{151}\text{Eu}^{3+}$ isotope [1]. Throughout this thesis, only the stoichiometric complex with natural isotopic abundance was synthesized and examined. Due to the high quantity of material required for our recrystallization method, multiple synthesis attempts were performed, most of which were successful.

4.3.1.2. Recrystallization of $[\text{Eu}(\text{BA})_4(\text{pip})]$ for ensemble spectroscopy

The macroscopic single crystals of the Eu^{3+} -based molecular complex were grown using the slow-evaporation method, a widely used technique for crystallizing dissolved molecular materials [62, 119]. The crystals proved to be soluble in acetone and ethanol.

³⁵ Model: B11907-10G for 1-phenylbutane-1,3-dione, 411027-100ML for piperidine, and 203254-5G for $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, purchased from Sigma-Aldrich.

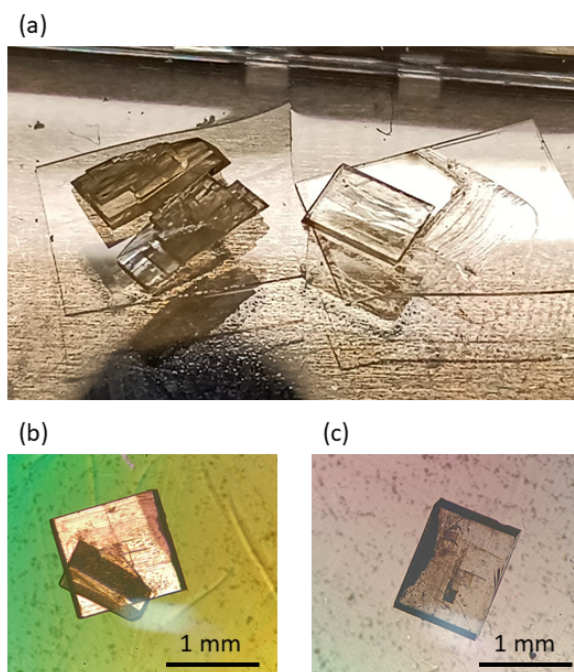


Figure 4.14: Macroscopic SKR520 crystals grown by recrystallization. (a) Crystals several millimeters in size obtained after recrystallization. (b) and (c) Microscope images of single crystals used for X-ray diffraction measurements. The monoclinic crystal structure was confirmed via the X-ray diffraction analysis. Scale bars indicate approximate crystal sizes.

The process involved dissolving 125 mg of SKR520 nanocrystals in 6 mL of ethanol to form a near-saturated solution. After filtration through a $0.1\ \mu\text{m}$ syringe filter³⁶ to minimize the number of nucleation sites, the solution was transferred to a clean beaker and covered with aluminum foil perforated with small holes to enable controlled slow evaporation of the solvent [62, 119]. The beaker is preferably kept undisturbed in a low-vibration environment for approximately one week, yielding several millimeter-sized large crystals. The largest crystal to date, as shown in Figure 4.14(a), measured lateral sizes of $3.3\ \text{mm} \times 2.6\ \text{mm}$ with a thickness of $\approx 400\ \mu\text{m}$. These macroscopic single crystals are advantageous for ensemble spectroscopy due to reduced scattering losses during light collection and improved structural order compared to powder-like samples [62]. In addition, two randomly selected macroscopic crystals, depicted in Figure 4.14(b) and (c), were analyzed using X-ray diffraction measurements to verify that the crystal had crystallized in the correct lattice structure and symmetry. For both samples, the monoclinic crystal lattice could be clearly confirmed, supporting our focus on further characterization measurements on such geometries.

³⁶ Model: Millex-VV syringe filter unit, purchased from Carl ROTH.

4.3.1.3. High-resolution optical characterization of different forms of $[\text{Eu}(\text{BA})_4(\text{pip})]$

This section summarizes and presents the key results. We have chosen to follow the chronological sequence of the obtained findings, as they were acquired across various measurement series, cooling procedures, sample batches, and sample geometries. Therefore, a brief explanation of the investigated samples is provided next, which are listed in Table 4.1. The table outlines which measurements were performed with each sample, the corresponding synthesis batch, the sample morphology, and the temperature conditions under which the measurements were conducted. For the final two samples, the existing setup was extended with an RF coil, enabling primarily spin-characterization measurements. Another important aspect is the sample preparation. For each measurement series, a new sample was typically prepared by incorporating the powder or single crystals into our fiber-based ferrule sample holder. The amount of powder used cannot be measured quantitatively, and in some cases, insufficient amounts of powder were added, or the powder was not compressed using a fiber, leading to minor variations between measurements. Additionally, the experimental parameters were optimized from one series to the next, resulting in the most recent measurements being especially promising and consistent with the published results [1]. During sample insertion, care must be taken to avoid mechanical damage to the crystals, as this can introduce additional strain and structural disorder. On the other hand, the amount of material loaded is critical for achieving sufficient optical depth to obtain strong absorption signals. All mentioned samples possess a stoichiometric Eu^{3+} composition with natural isotopic abundance (100 % Eu^{3+} doping concentration and both isotopes). The following paragraphs introduce the central SKR520 samples and explain the approach taken for each subsequent step.

SKR 520 Sample 1: The first sample consisted of crystalline powder from the initial synthesis batch, with grain sizes reaching up to $200\text{ }\mu\text{m}$ (close to the ferrule diameter). During sample preparation, only minimal amounts were loaded into the sample space of the pulled-back fiber ferrule to reduce scattering losses. Figure 4.15(a) and (b) present the room-temperature emission spectrum of the investigated sample 1, where the characteristic transitions of trivalent europium are clearly observed. The coherent $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition at the emission wavelength 579.972 nm (vacuum) appears promising in terms of its narrow linewidth of $(0.169 \pm 0.006)\text{ nm}$, which is in excellent agreement with the previously published values [1]. However, its branching ratio is relatively low at only 0.16 %, which is suboptimal for quantum applications and would definitely require cavity-mediated enhancement to reach high coherent emission rates [34]. Figure 4.15(c) shows the excited-state lifetime of the $^5\text{D}_0$ level, from which an optical lifetime $T_{1,0} = (520.12 \pm 0.54)\text{ }\mu\text{s}$ was extracted by fitting the data to a monoexponential decay. This result is in good agreement with the published optical lifetime of $T_{1,0} = 540\text{ }\mu\text{s}$. From our experience, the deviation from this reported value primarily depends on the sample preparation method, but the current synthesis and sample filling procedure are consistent across several trials with obtained maximum discrepancies

Table 4.1: Overview of investigated SKR520 samples. The table summarizes the performed measurements, corresponding synthesis batch, sample morphologies, and measurement temperatures for each sample. The last column contains information on RF measurements and is only relevant for the final two samples.

Sample	Sample batch	Morphology	Temperature	Measurement types	RF-based measurements
SKR520 Sample 1	first batch	powder	4.2 K, exchange gas dipstick	spectra, optical life-time, inhomogeneous linewidth, SHB, spin lifetime, temperature dependence	-
SKR520 Sample 2	second batch	powder	4.2 K, transfer line dipstick	spectra, optical life-time, inhomogeneous linewidth, SHB, spin lifetime	-
SKR520 Sample 3	recrystallized from second batch	macroscopic crystal	< 100 mK, Sionludi confocal setup	spectra, inhomogeneous linewidth, SHB	prepared but not used
SKR520 Sample 4	recrystallized from second batch	macroscopic crystal	< 200 mK, Sionludi	spectra, optical life-time, inhomogeneous linewidth, SHB, spin lifetime	-
SKR520 Sample 5	third batch	powder	< 200 mK, Sionludi	inhomogeneous linewidth, SHB, spin lifetime	-
SKR520 Sample 6	third batch	powder	4.2 K, exchange gas dipstick	FID, photon echo	ODNMR (coil 1)
SKR520 Sample 7	recrystallized from third batch	macroscopic crystal	4.2 K, flange dipstick	FID, photon echo, three-pulse photon echo, spin lifetime	-
SKR520 Sample 8	recrystallized from third batch	macroscopic crystal	4.2 K, flange dipstick	inhomogeneous linewidth, spectral tailoring, spin lifetime	ODNMR, Rabi oscillations, spin echo, CPMG (coil 2)

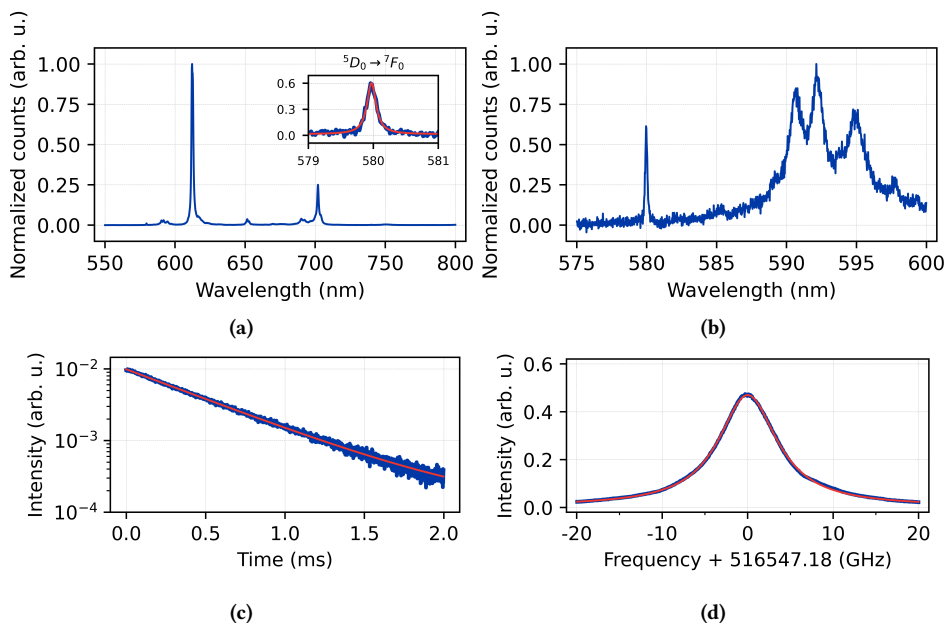


Figure 4.15: Initial optical characterization of SKR520. (a) Room-temperature PL spectrum showing all resolved $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions up to $J = 5$. The inset illustrates a Lorentzian fit of the emission spectrum of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition centered around 579.972 nm, with a FWHM of (0.169 ± 0.006) nm. (b) Zoomed-in view of the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions. The branching ratio of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is about 0.16 % and is relatively low compared to other REI-based systems. Both spectra are normalized to their respective maximum intensities. (c) Measured excited-state lifetime $T_{1,0}$ of SKR520 at room temperature. The data are fitted with a monoexponential decay function on a logarithmic y-scale, yielding an optical lifetime $T_{1,0}$ of (520.12 ± 0.54) μs . (d) High-resolution PLE scan of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition showing the inhomogeneous line profile. The PLE measurement reveals a linewidth of approximately (8.37 ± 0.01) GHz at a temperature of 4.2 K.

of 10 %. In the absence of pure dephasing, the fundamental lifetime-limited linewidth $\Gamma_h = 1/(2\pi T_{1,0})$ is on the order of approximately 295 Hz [1]. Figure 4.15(d) illustrates a photoluminescence excitation (PLE) scan over the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition, centered at 580.378 nm, which corresponds to 516 547.18 GHz. The measured inhomogeneous linewidth is about (8.37 ± 0.01) GHz, equivalent to a linewidth of approximately 0.009 nm, which is slightly broader than the 6.6 GHz (≈ 0.007 nm) reported in [1]. This result constituted the narrowest inhomogeneous linewidth achieved in this measurement series, while the typical values obtained for powder samples ranged between 10 GHz to 20 GHz. The narrow linewidth and the Lorentzian line shape thus indicate a high crystalline quality and low structural disorder of the sample. Nonetheless, no significant absorption signal could be observed, potentially due to the limited amount of absorbing material introduced into the ferrule sample holder.

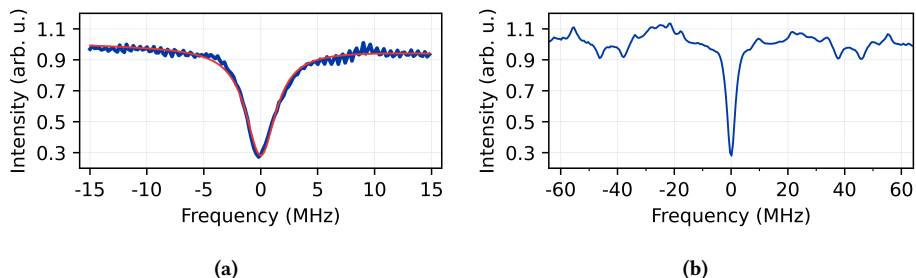


Figure 4.16: SHB measurements of SKR520. (a) Fluorescence-detected spectral hole with a measured linewidth of (3.23 ± 0.06) MHz, extracted from the Lorentzian fit (red). (b) Broader SHB spectrum with increased resolution obtained with optimized parameters, revealing additional side features such as anti-holes and side holes, indicating population redistribution among the ground-state hyperfine levels. Both measurements were performed at a temperature of 4.2 K.

In order to access the homogeneous linewidth within the inhomogeneous broadening, coherent ensemble spectroscopy was performed at a cryogenic temperature of 4.2 K in the exchange gas dipstick. The typical approach involves, in a first step, SHB measurements to identify the appropriate pulse parameters and laser power levels, as they can differ for the specific molecular compounds under investigation, followed by pulsed photon echo schemes. However, during this measurement series, photon echo experiments could not be successfully implemented and were only performed and optimized in subsequent campaigns. Published values for the SKR520 molecular complex report an optical coherence time $T_{2,o}$ of about $10.5 \mu\text{s}$ of the $^5\text{D}_0 \leftrightarrow ^7\text{F}_0$ transition corresponding to a homogeneous linewidth of $\Gamma_h = 1/(\pi T_{2,o})$ of around 30.2 kHz. For an ion concentration of 100 %, this value is among the most promising reported for molecular complexes [35]. In our measurements using SHB, the narrowest observed spectral hole at the time exhibited a width of about (3.23 ± 0.06) MHz, as shown in Figure 4.16(a). This corresponds to a homogeneous linewidth of approximately (1.66 ± 0.03) MHz, which is related to a pure dephasing time $T_{2,o}^*$ of (192 ± 4) ns. Furthermore, through initial optimization of the pulse parameters, first broad spectral range scans were successfully performed, enabling the resolution of side holes and anti-holes, which are illustrated in Figure 4.16(b). The quality, however, is not yet sufficient to perform a reliable fit to extract the hyperfine structure of the corresponding isotope of the molecular compound, as not all features are resolved or captured.

To investigate the spin dynamics, spectral hole depth measurements were conducted as a function of the delay time between burn and readout pulses of the SHB sequence, as shown in Figure 4.17(a). The resulting decay curve revealed a hyperfine lifetime of approximately (104.31 ± 9.38) s, which is promising for potential coherent nuclear spin control. In general, significantly longer relaxation times have been reported for other material platforms [67, 120]. For the SKR520 molecular complex, two distinct decay components were observed: a short one of 430 ms and a longer one of around 5 min. The deviation from the previously reported value may be attributed to sample preparation

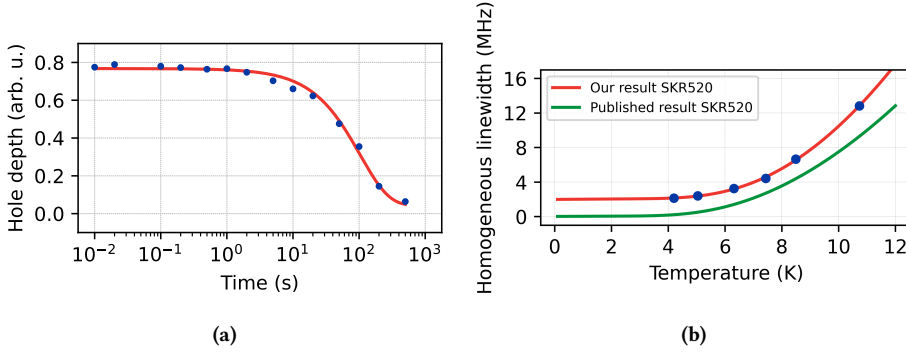


Figure 4.17: Hyperfine lifetime and temperature-dependent optical dephasing of SKR520. (a) Decay of the spectral hole depth measured at a temperature of 4.2 K is fitted with a monoexponential function, revealing a time constant of $T_{1,s} = (104.31 \pm 9.38)$ s. This component may be attributed to the long decay constant, while the fast component was probably too short to be measured in this case. (b) Homogeneous linewidth Γ_h as a function of temperature (blue dots), extracted via SHB measurements up to approximately 10 K. The fitted curve (red) shows a linear increase in linewidth at temperatures below 6 K, indicative of coupling to TLSs. Above this temperature, a steeper exponential rise is observed, potentially originating from phonon-mediated dephasing processes via coupling with quasi-localized vibrational LFM. In comparison to the reported results (green curve) in Ref. [1], the shape of the curve is very similar, with the only difference appearing in the constant offset along the x-axis.

differences or to possible temperature gradients during the measurements, as it was performed using an exchange gas dipstick, where thermalization issues can occasionally occur. The presence of two time constants was consistently observed in subsequent measurement series. Although the obtained absolute values of the hyperfine lifetimes varied, they remained in the same order of magnitude.

In addition, temperature-dependent measurements of the homogeneous linewidth, carried out via SHB, provided more insights into the dominant dephasing mechanisms. As introduced in Section 2.2, two different temperature regimes can be identified. According to Serrano *et al.* [1], temperatures below 3.5 K show a linear temperature dependence consistent with TLS-induced dephasing, whereas at higher temperatures, quasi-localized LFMs governed the dephasing behavior, which is described by an exponential increase of the homogeneous linewidth. At even higher temperatures above 10 K, Raman phonon processes take over and contribute to $\propto T^7$ scaling. The data can be modeled by using the expression [1, 61]:

$$\Gamma_h(T) = \Gamma_0 + \Gamma_{\text{TLS}} + \Gamma_{\text{LFM}} \approx \Gamma_0 + \alpha_{\text{TLS}}T + \alpha_{\text{LFM}}e^{-\frac{\Delta E_{\text{LFM}}}{k_B T}}. \quad (4.3.1)$$

The model was used to describe fluorescent chromophore molecules exposed to amorphous materials, and featured exactly the same temperature-dependent behavior within temperatures below 10 K [61]. In order to perform a fit to our SHB data, we utilized

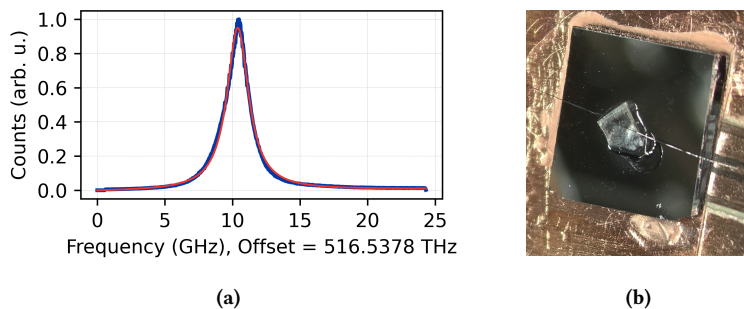


Figure 4.18: Cryo-confocal measurements on a macroscopic SKR520 crystal. (a) Image of the SKR520 single crystal positioned on the sample holder of the cryo-confocal setup, which is thermally anchored to the cold plate of the cryostat. (b) Measured inhomogeneous linewidth of the $^5\text{D}_0 \leftrightarrow ^7\text{F}_0$ transition, recorded within the cryo-confocal microscope setup. The observed linewidth of (1.95 ± 0.01) GHz is narrower than the reported value [1]. The PLE scan was performed at a temperature of 4.2 K.

the fit parameters of [1]. Figure 4.17(b) shows the result compared in good agreement with the published fit. The slight difference (constant x-axis offset) may arise again from temperature variations within the dipstick cryostat. The data are fitted with the previously introduced function in Equation 4.3.1, yielding the parameters $\Gamma_0 = 1.98$ MHz, $\alpha_{\text{TLS}} = 23$ kHz K $^{-1}$, $\alpha_{\text{LFM}} = 234$ MHz, and $\Delta E_{\text{LFM}} = 711$ GHz. Although all parameters exhibit high uncertainties, they are all relatively close to the reported values. Only the extrapolated residual homogeneous linewidth of 1.98 MHz at 0 K strongly deviates from the estimated 8 kHz in Ref. [1]. These results should be validated through additional measurements to confirm their correctness and reproducibility. Furthermore, the extrapolated linewidth Γ_0 is still limited, particularly by Eu^{3+} ion-ion interactions in highly doped samples. It was shown that upon dilution with Y^{3+} ions (25 % Eu^{3+} concentration) the optical coherence time could be significantly increased up to 65 μs , which is a record value among the investigated molecular materials [35].

In the following, SKR520 sample 2 is omitted, as it was only used for pulse parameter optimization in SHB studies and for the development and testing of new sample holders and preparation methods, respectively.

SKR520 samples 3, 4 and 5: These three samples are summarized together, as all were measured inside dilution refrigerators. Following successful recrystallization attempts, which yielded macroscopic crystals, it became important to characterize their optical properties and compare them to the already published data.

SKR520 sample 3 was measured using the cryo-confocal setup in the working group of **Professor Wolfgang Wernsdorfer**. The sample is depicted in Figure 4.18(a). A wire bonded across the sample was intended for later RF excitation, but was not applied during

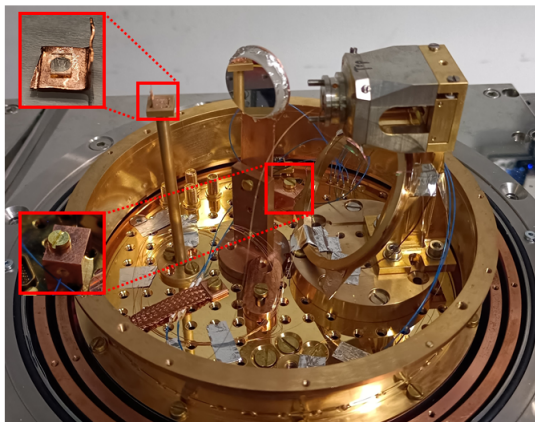


Figure 4.19: Integration of different sample types into the Sionludi cryostat. The image highlights the mounting positions and the integration methods used. The powder-like sample is incorporated in a fiber-coupled copper block (lower-left red box), which is screwed directly to the cold plate to ensure good thermal contact. In contrast, the macroscopic crystal is glued to a copper plate (upper-left red box), which in turn is mounted to a copper post to allow for free-space optical access. Excitation light is directed onto the sample via the stationary mirror, and the transmitted signal is collected outside the cryostat.

this measurement series. As shown in Figure 4.18(b), the inhomogeneous linewidth was found to be as narrow as (1.95 ± 0.01) GHz, approximately a factor of three narrower than the published value [1]. This strongly suggests that the crystalline structure in these macroscopic crystals exhibits superior order compared to fine powder-like samples or microcrystalline powder. Initial SHB measurements at millikelvin temperatures were also performed, but no significant changes in the hole linewidth were observed. However, it is important to state that the experimental parameters were not yet optimized for this setup and geometry. In the confocal setup, the sample is excited at a tightly focused spot with a point-spread function of less than $1\text{ }\mu\text{m}$, meaning that pulse parameters from conventional SHB measurements cannot be directly applied, and excitation powers need to be adjusted accordingly. The most notable observation was that individual spectral holes persisted over extended periods (up to 30 min) and even appeared at spatially different positions. At that time, no conclusive explanation could be provided for this side effect. Nevertheless, the finding that macroscopic crystals show promising optical properties required further investigation.

Therefore, the two SKR520 samples 4 and 5 were mounted in our own Sionludi cryostat: one powder-like sample incorporated into a copper block, and one macroscopic crystal attached to a copper holder designed for free-space excitation and collection measurements. Figure 4.19 shows the implementation of both sample holders, including an additional mirror to guide the light toward the output window and thus to the detector. The goal was a systematic comparison of the two geometries under millikelvin

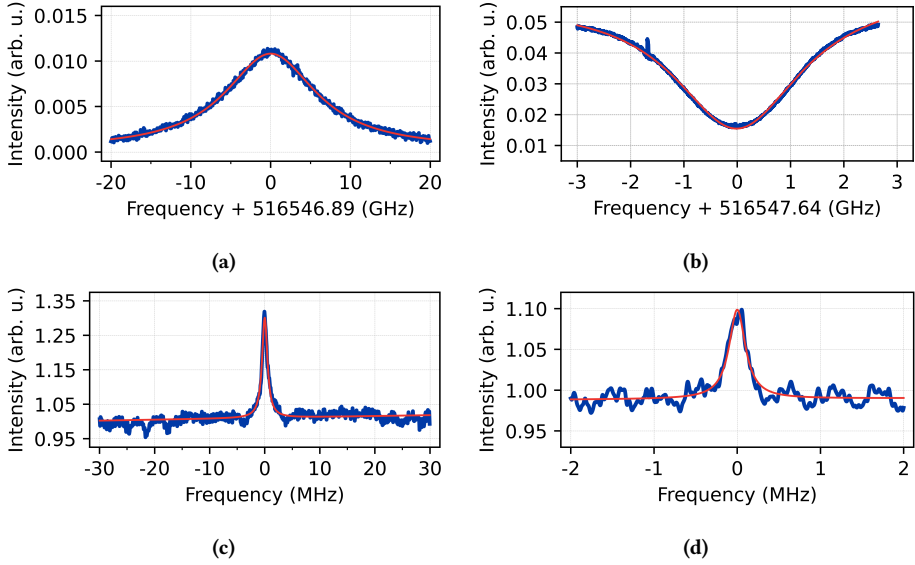


Figure 4.20: Comparison of optical properties between powder and macroscopic crystal samples of SKR520 at millikelvin temperatures. (a) PLE scan of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition for the powder-like sample revealing an inhomogeneous linewidth of approximately (13.93 ± 0.06) GHz, which is in the expected range between 10 and 20 GHz observed in previous measurements on SKR520. (b) Transmission scan of the same transition but for the macroscopic crystal. The fit (red curve) yields a much narrower inhomogeneous linewidth of about (2.91 ± 0.01) GHz, thereby confirming our assumptions and results on macroscopic crystalline samples. The small peak on the left side of the profile is attributed to a residual burned spectral hole from a previous measurement that still persisted over time. (c) SHB measurement on the powder sample, yielding the narrowest spectral hole measured for this morphology, recorded at an excitation power of $21 \mu\text{W}$. A Lorentzian fit to the data results in a spectral hole width of (1.17 ± 0.04) MHz, with a contrast of approximately 30 %. (d) Spectral hole measured on the macroscopic crystal, representing our narrowest recorded linewidth so far. A Lorentzian fit yields a spectral hole width of (0.24 ± 0.01) MHz, with a contrast of about 10 %. Both SHB measurements were carried out by detecting the transmission signal. All measurements were performed at a temperature of ≤ 100 mK.

conditions (≤ 100 mK). In these experiments, both the inhomogeneous linewidths and spectral holes were measured. For both geometries, the expected results could be reproduced, as depicted in Figure 4.20(a) and (b). A narrow inhomogeneous linewidth of (2.91 ± 0.01) GHz was observed for the second recrystallized macroscopic crystal, while the powder sample showed a broader linewidth of around (13.93 ± 0.06) GHz but one comparable to previous results. Nonetheless, the spectral holes, which are represented in Figure 4.20(c) and (d), were significantly improved for both sample types, yielding linewidths of (1.17 ± 0.04) MHz and (0.24 ± 0.01) MHz, respectively. Both SHB measurements represent our narrowest recorded spectral holes to date for these geometries,

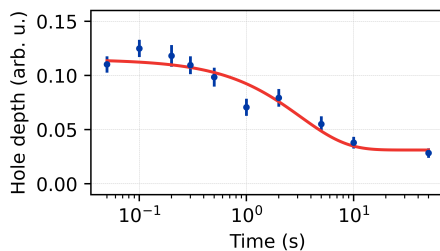


Figure 4.21: Hyperfine lifetime of the macroscopic crystal. Spectral hole depth decay as a function of the delay time between burn and probe pulses. The data are fitted with a single exponential decay function, yielding the fast relaxation component of the hyperfine lifetime $T_{1,s(\text{short})} = (3.19 \pm 0.98)$ s. Since no slow relaxation component was observed within the measured delay time up to 50 s, it is likely that an even longer hyperfine lifetime component exists beyond this timescale. All measurements were performed at a temperature of about 100 mK.

and the latter now agrees well with the previously published values in Ref. [1]. It should be noted that both SHB measurements were conducted via detecting the transmission signal, and in addition to averaged SHB experiments, single-shot measurements were performed to avoid power broadening, with excitation powers around 20 μW .

However, the hole lifetime was only investigated for the macroscopic crystal, as the signal strength from the powder sample within the copper block was too weak. The design of the copper block is different from the conventional fiber-based ferrule sample holder, which affected the sample preparation and potentially increased scattering losses. Longer delay times would have required higher excitation powers, but this in turn led to significant power broadening, and the signal became too noisy to extract meaningful data. Figure 4.21 shows the measured hyperfine lifetime for the macroscopic crystal at a temperature of about 100 mK, which was approximately (3.19 ± 0.98) s. Up to a delay time of 50 s, no second decay component was observed, suggesting that the corresponding relaxation time constant could be very long and likely remains undetectable at these low temperatures, as described in Könz *et al.* [67]. Furthermore, it was not possible to achieve a high spectral hole contrast without excessive warming of the sample. A compromise had to be found between contrast, excitation power, and thermalization. The macroscopic crystal was glued onto the copper holder, which does not offer an ideal thermal contact. Strong excitation pulses can generate phonons in the ligand field of the molecular complex that are longer-lived than in rigid crystal lattices, and these intense pulses were found to cause heating, with the cryostat returning to millikelvin temperatures very slowly. Up to this point, no photon echoes could be observed.

SKR520 sample 6 and 7: The next two samples were prepared with the aim of measuring further coherent optical signals. The SKR520 sample 6 was prepared using powder filled into bare ferrules which were incorporated into a ceramic casing. The sample holder

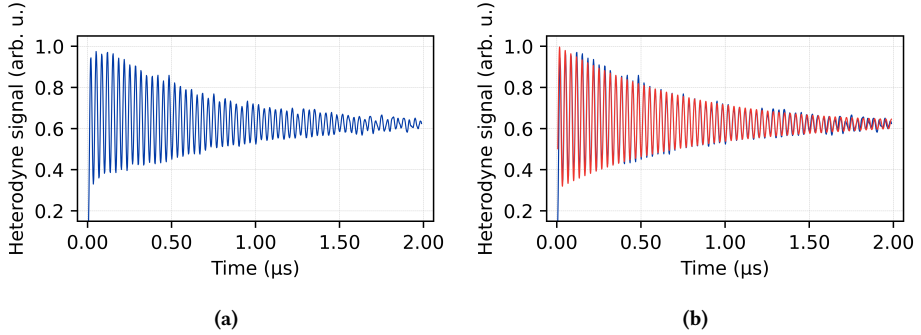


Figure 4.22: FID measurement of SKR520. A strong $4\ \mu\text{s}$ burn pulse of $170\ \text{mW}$ optical power is applied to a powder-like sample, followed by a frequency-detuned $10\ \mu\text{s}$ readout pulse, yielding a heterodyne-detected beating signal. **(a)** Raw FID signal showing the interference pattern without a fit, in order to highlight the clear oscillatory behavior of the coherent beating. **(b)** Fitted FID signal (red curve) using an exponentially decaying envelope with a background function, resulting in a dephasing time $T_{2,\text{o(FID)}}^*$ of about $(728 \pm 18)\ \text{ns}$. The measurement was performed at a temperature of $4.2\ \text{K}$.

was installed in our exchange gas dipstick, with the intention of eventually integrating it into our RF coil for initial spin-characterization measurements. As the SKR520 sample 7 involved a macroscopic crystal, we modified our fiber-based ferrule setup and introduced an asymmetric design in order to provide enough space for millimeter-scale samples. This sample holder was integrated into a flange dipstick model, enabling simultaneous measurements.

After performing a parameter sweep for the optical $\pi/2$ and π pulses, a significant beating signal was observed in several readout pulses, resulting from the heterodyne technique. The subsequent fast Fourier transform (FFT) revealed the correct detuning frequency of $30\ \text{MHz}$. This marked a final breakthrough toward full optical characterization. Since the measurements are carried out on ensembles, there is a broad distribution of potential Rabi frequencies. Therefore, the pulse parameters were chosen primarily based on the published schemes [1]. During photon echo measurements, care must be taken: when applying short delay times between $\pi/2$, π pulses, and readout pulses, the detected beating signal may originate from an FID signal, which represents the dephasing of the excited dipoles. Figure 4.22 shows such a heterodyne-detected optical FID signal measured on the powder sample. The excitation was performed using a $4\ \mu\text{s}$ $\pi/2$ excitation pulse at an optical power of $170\ \text{mW}$, followed by a $10\ \mu\text{s}$ readout pulse. The resulting beating signal, caused by the interference between the residual FID emission and the frequency-detuned probe pulse, is clearly visible. To avoid the saturation of the APD, the signal was attenuated before detection. Figure 4.22(a) illustrates the raw beating signal without a fit to emphasize the decay of the coherent oscillations. The data are fitted with a sum of an exponentially decaying sinusoidal function and a saturation

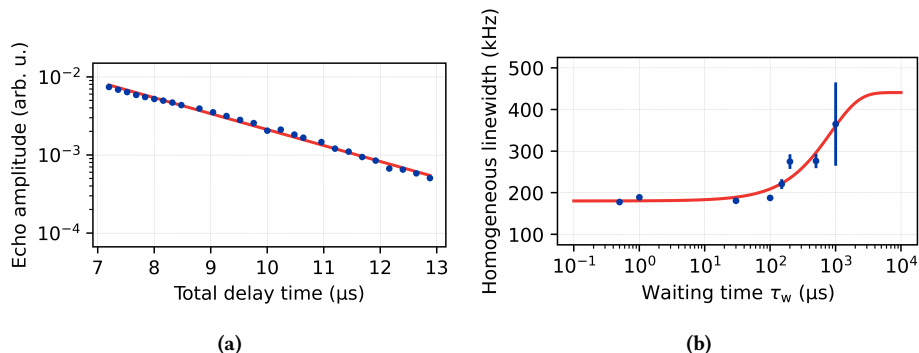


Figure 4.23: Photon echo measurements of SKR520. (a) Two-pulse photon echo decay as a function of the total delay time, yielding an optical coherence time $T_{2,o}$ of about $(2.13 \pm 0.03) \mu\text{s}$. A linear fit (red line) was applied to the data on a logarithmic y-scale to extract the decay constant. The echo amplitude was detected via heterodyne detection and analyzed using an FFT. (b) Three-pulse photon echo signals measured at various waiting times τ_w between the second and third $\pi/2$ pulses to investigate spectral diffusion. The resulting data is displayed as homogeneous linewidths over the waiting time τ_w , showing an increase due to time-dependent spectral broadening caused by the local environment. The data are fitted using the sudden-jump diffusion model [1], yielding a broadened linewidth of $(521 \pm 12) \text{ kHz}$, where the unweighted fit is shown for clarity. All measurements were performed at a temperature of 4.2 K.

function of the form $(c \cdot x + f)/(e + x)$ as the background, yielding an optical dephasing time $T_{2,o(\text{FID})}^*$ of about $(728 \pm 18) \text{ ns}$. The resulting fit is represented in Figure 4.22(b).

As a consequence, the following photon echo sequences were programmed with initial delay times longer than the $T_{2,o}^*$ to ensure that no FID contributions interfered with the readout signal. Figure 4.23(a) presents a two-pulse photon echo measurement on the powder sample, where the echo amplitude, extracted via a heterodyne-detection readout pulse and Fourier analysis, is plotted as a function of the total delay time. The experiment was conducted using $\pi/2$ and π pulses of equal duration ($2 \mu\text{s}$), since a large ensemble is probed and the distribution of Rabi frequencies ensures that a fraction of the ions undergo the desired rotation. Each optical pulse was applied with an excitation power of approximately 93 mW. A linear fit to the data on a logarithmic y-scale yields an optical coherence time $T_{2,o}$ of about $(2.13 \pm 0.03) \mu\text{s}$. The longer coherence times reported in Ref. [1] for this molecular system were obtained at a temperature of 1.45 K with an excitation power of 300 mW. According to the temperature-dependent model provided in that study, the expected coherence time at 4.2 K is around $1.28 \mu\text{s}$, which is in good agreement with our measurements at this temperature. To achieve potential improvements, measurement series were conducted using various samples, including SKR520 sample 7, within the newly developed asymmetric sample holder. In this configuration, the optical coherence time $T_{2,o}$ could be slightly increased to approximately $3 \mu\text{s}$. However, the data quality was lower, with fewer recorded measurement points, likely due to laser instabilities present at the time of the experiment.

Additionally, three-pulse photon echo measurements were performed on a macroscopic SKR520 crystal to investigate spectral diffusion effects. The difference compared to two-pulse photon echoes lies in the separation of the π pulse into two $\pi/2$ pulses. At zero waiting time between both $\pi/2$ pulses, the measurement constitutes a conventional photon echo scheme. By increasing the waiting time, the interaction of the dipoles with the surrounding environment is probed at time scales longer than the $T_{2,0}$. The longer the waiting time, the more dephasing is accumulated. Figure 4.23(b) illustrates the broadening of the homogeneous linewidth up to (521 ± 12) kHz when experiencing spectral diffusion during the increasing waiting time τ_w between the $\pi/2$ pulses. Each data point was measured with a three-pulse photon echo sequence. The detection procedure and data analysis are analogous to the two-pulse photon echo experiments. For clarity, the unweighted fit is shown in Figure 4.23(b), as it provides a visually consistent description of the data trend. A weighted fit using the experimental uncertainties does not adequately describe the data, likely due to an overestimation of the individual data point uncertainties or increased scatter in the data. Further measurements with improved SNR are therefore required to enable a meaningful analysis of the underlying dephasing mechanism. However, the extracted parameters remain within the same order of magnitude and do not qualitatively affect the physical interpretation. The data are fitted using the *sudden-jump diffusion model* [121]:

$$\Gamma_h = \Gamma_0 + \frac{1}{2}\Gamma_{\text{SD}} \left(1 - e^{-R\tau_w}\right), \quad (4.3.2)$$

where R denotes the flip rate (changes in the local environment), Γ_0 the homogeneous linewidth defined through the model at the waiting time $\tau_w = 0$, and Γ_{SD} the spectral diffusion linewidth contribution. Spectral diffusion is attributed to the presence of paramagnetic spin impurities in the molecular crystals [1]. However, at this stage, the focus shifted toward the investigation of spin properties, as a dedicated dilution refrigerator with an exchange gas chamber is planned for future ensemble spectroscopy to enable better thermalization and thus improve optical coherence times.

4.3.1.4. Characterization of spin properties via combined optical and RF control

This section follows the previous one and describes the progress made during the spin measurements. Two SKR520 samples 6 and 8 were investigated: the first was powder-based, and it was on this sample that the first ODNMR signal was observed using the exchange gas dipstick. The second was a macroscopic crystal, which was integrated into our flange dipstick and immersed in liquid helium. Under these conditions, a complete spin characterization, including coherent spin control, was successfully demonstrated. Due to the differing sizes of the sample holders, two separate RF coils were produced to incorporate each geometry.

SKR520 sample 6: It should be noted at this point that during the measurement period for this sample, we initially employed a custom-built high-power amplifier, which

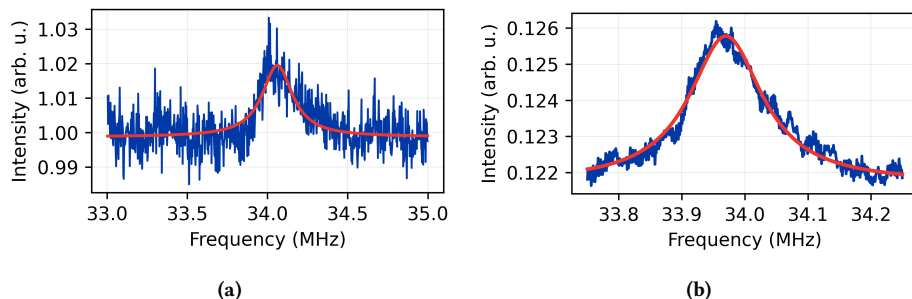


Figure 4.24: Initial CW ODNMR measurements of the 34 MHz hyperfine transition of SKR520. (a) CW ODNMR measurement sequence applied on the 34 MHz hyperfine transition in order to probe the spin inhomogeneity. The RF frequency is swept with a chirp rate of 1 MHz s^{-1} , while simultaneous optical pumping reveals the spin inhomogeneous line in the collected fluorescence signal. The data are fitted with a Lorentzian function (red curve), yielding a spin linewidth of $(230 \pm 16) \text{ kHz}$. (b) Improved spectral resolution obtained using a modified sequence (chirp rate of 50 kHz s^{-1}), resulting in a narrower spin inhomogeneous line, with a width of $(143 \pm 3) \text{ kHz}$ (red curve). In both cases, the resonance position corresponds to the hyperfine spin transition within the $J = 0$ manifold of the $^{151}\text{Eu}^{3+}$ isotope. Both measurements were performed at a temperature of 4.2 K.

unfortunately failed after only a few hours of operation and was replaced with a commercial unit. Approximate parameters and a principal understanding of the scheme were taken from the PhD theses of Cyril Laplane and Alexander Lovrić [99, 122], both of whom demonstrated coherent spin control of Eu^{3+} ensembles in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$. A Raman heterodyne detection technique, comparable to the method we used for detecting photon echoes, was applied in their work to measure several spin properties, such as the linewidths of the two hyperfine splittings.

In our case, we chose to detect the spin state via the fluorescence signal, corresponding to the population of the excited ions. This readout scheme does not require additional effort and is considered an equivalent principle compared to the Raman heterodyne detection, although slight differences in sensitivity may exist. The LC circuit was adjusted according to the hyperfine structure from the reported work [1] and was also independently confirmed through our own simulations. The first measurable signal, as shown in Figure 4.24(a), was obtained using CW excitation of the 34 MHz hyperfine transition of the $^{151}\text{Eu}^{3+}$ isotope at an RF power of $\approx 230 \text{ mW}$. The choice of utilizing this transition was made arbitrarily, however, for the recent sample, both hyperfine transitions were analyzed. The measured resonance linewidth is about $(230 \pm 16) \text{ kHz}$, but with a very low contrast. The crucial factor for observing a clear signal is achieving a good spin state preparation at the beginning of the measurement. The population difference between two levels involved in the probed hyperfine transition directly determines the observed signal contrast [123]. A two-pulse technique was employed: a first optical pulse at a constant frequency was used to depopulate a specific spin

state level, followed by a second optical pulse, after a short delay, with a simultaneous frequency chirp of the RF signal to probe the spin inhomogeneous line. The short interruption between the pulses caused a transient feature in the readout signal due to re-burning of the spin state, making the evaluation more difficult.

To improve the signal, both pulses were merged into a continuous sequence, and the RF coil was turned on at a defined point in time. This significantly enhanced the signal quality, resulting in a narrowed linewidth of (143 ± 3) kHz, as illustrated in Figure 4.24(b). It is important to find a proper balance between chirp rate and laser power levels to ensure that the spin inhomogeneous line is not affected by other mechanisms and appears Lorentzian as well as symmetric. If one of those parameters is not well-adjusted, the falling edge of the signal (in the direction of the chirp) exhibits an exponential decay, as the laser begins to re-initialize the spin state. Typical chirp rates are around 100 kHz s^{-1} , while the first and coarse scans were performed with 1 MHz s^{-1} at optical powers of a few $10 \text{ }\mu\text{W}$ to 20 mW . The latter measurement was obtained by applying an RF power of 1 W . However, compared to $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$, the measured linewidths are about one order of magnitude higher. Future steps will involve applying the Raman heterodyne readout technique to potentially improve the signal quality.

SKR520 sample 8: The final investigated sample was a macroscopic crystal incorporated in an asymmetric sample holder configuration. This millimeter-scale crystal originated from early recrystallization trials and was initially integrated to test our newly developed measurement techniques. Even though the PLE scan revealed a broad inhomogeneous linewidth of $(23.10 \pm 0.09) \text{ GHz}$, as shown in Figure 4.25(c), we continued the spin measurements, despite earlier samples exhibiting significantly narrower lines. However, it became clear that even a test crystal could yield valuable experimental results.

In the beginning, spectral tailoring attempts were carried out on this crystal. As previously discussed, efficient class preparation is crucial for obtaining strong signal contrast. Although more advanced techniques such as those introduced by Nilsson and Lauritzen *et al.* [79, 98] for preparing isolated ion classes were not fully implemented due to time constraints, the high optical depth of the crystal allowed us to adjust our parameters and initiate preliminary class preparation trials. Figure 4.25(a) shows four anti-holes re-appearing within a spectral pit after burning at a frequency offset of 21.5 MHz (corresponding to the hyperfine splitting), indicating the partial preparation of spin subclasses. The measurement was performed by detecting the fluorescence signal. Nonetheless, this does not constitute full class preparation, but it demonstrates the progress toward signal improvement. Figure 4.25(b) illustrates the equivalent result in transmission, however, the signal quality is slightly lower, which is the reason why the fourth anti-hole is not resolved. While only limited parameter optimization was applied in this case, the results indicate that further tuning could significantly improve the class preparation and thus also the quality of SHB measurements, enabling more accurate fitting and extraction of the hyperfine structure. To ensure that our new pulse sequences would not be limited by hyperfine lifetime, a final preparatory measurement was conducted, revealing two

4. Ensemble spectroscopy of Eu^{3+} -based molecular complexes

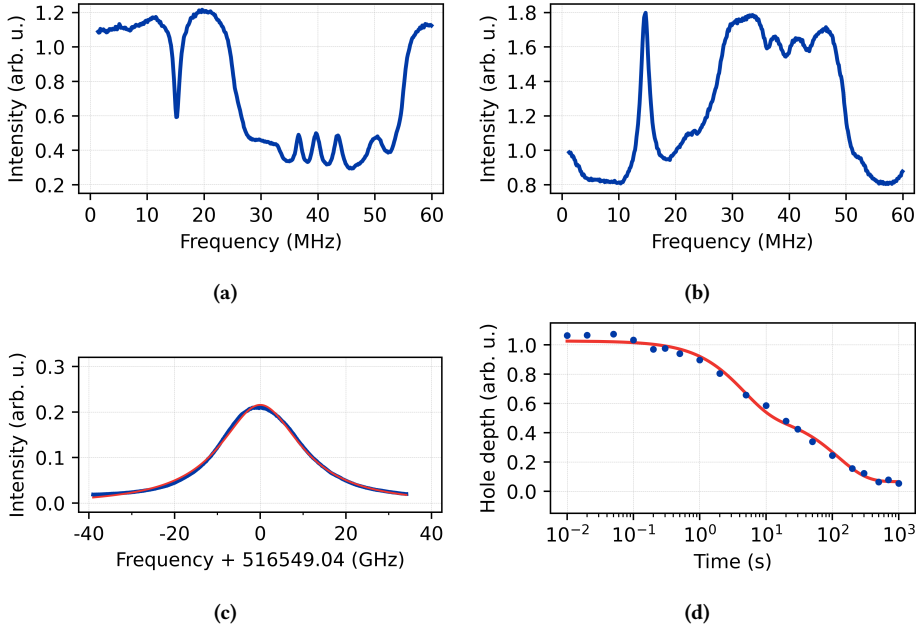


Figure 4.25: Preliminary measurements for spin characterization. (a) Spectral tailoring attempt by burning a spectral pit, selectively repopulating specific ion subclasses within the pit, shown in fluorescence detection. The single peaks do not denote a single ion class in this case. (b) Equivalent tailoring procedure measured in transmission, confirming population redistribution. (c) Inhomogeneous line scan measurement of the macroscopic crystal, demonstrating a rather broad linewidth of (23.10 ± 0.09) GHz (red curve). (d) The hole depth is shown as a function of delay time τ between burn and probe pulses. The data are fitted with a double-exponential function (red line), revealing two hyperfine spin relaxation times $T_{1,s(\text{short})} = (4.41 \pm 0.83)$ s and $T_{1,s(\text{long})} = (122.16 \pm 12.64)$ s, which are sufficiently long to perform coherent spin control experiments. All measurements were carried out at a temperature of 4.2 K.

long time constants ranging from (4.41 ± 0.83) s to (122.16 ± 12.64) s, as can be seen in Figure 4.25(d). As a consequence, all prerequisites were fulfilled to continue with the spin-characterization measurements.

Our refined pulse sequence now probes the spin inhomogeneous line point-by-point, beginning with the preparation of a single spectral pit with a width between 6 MHz to 10 MHz, followed by a 1 ms RF pulse (applied before the readout pulse), and concluding with an erasing sequence to reset the spin population for the next measurement. Each RF pulse was applied at a fixed frequency with a step size between 10 and 25 kHz to the next frequency step around the corresponding hyperfine transition. This sequence was tested on both hyperfine transitions. The 21.5 MHz transition consistently yielded a stronger, near-perfect Lorentzian response of the probed ensemble nuclear spin bath, while

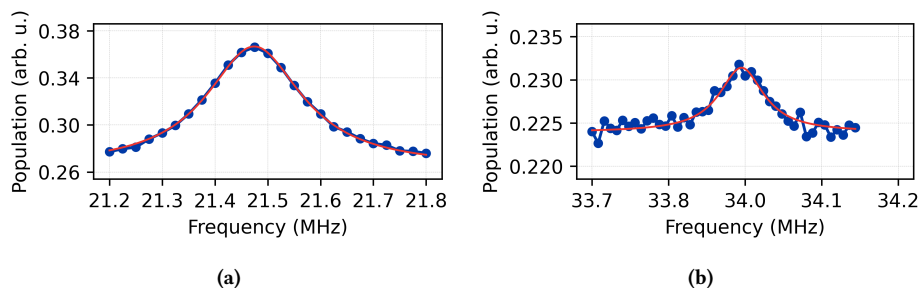


Figure 4.26: Spin inhomogeneous line of both hyperfine transitions of SKR520. (a) Fit with a Lorentzian function (red curve) to the first hyperfine transition at 21.5 MHz yields a linewidth of (221 ± 4) kHz. (b) Fit to the second hyperfine transition at 34 MHz shows a narrower but significantly weaker signal with a linewidth of (87 ± 8) kHz. This transition exhibits a weaker signal under identical experimental conditions, including optical power (~ 4.5 mW), RF power (~ 92.95 W), and pulse lengths.

the 34 MHz transition was comparably weaker under the same conditions including optical power of 4.5 mW, RF power of 92.95 W, and the same pulse sequence. Both fitted spin inhomogeneities of the hyperfine transitions are represented in Figure 4.26(a) and (b). Nevertheless, the linewidth could be confirmed with respect to the previous measurements. Given its promising performance, the 21.5 MHz transition was chosen for all subsequent measurements.

In a first step, a power series was recorded to study power broadening effects, as represented in Figure 4.27(a) and (b). The observed trend does not follow the typical square root behavior, however, the line was indeed power broadened and the narrowest mea-

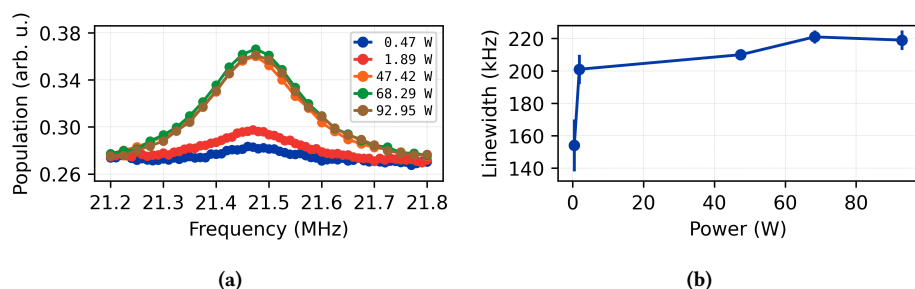


Figure 4.27: Power dependence of the 21.5 MHz hyperfine transition of SKR520. (a) ODNMR power series (power levels in inset), showing the evolution of the linewidth as a function of RF power. The data reveal power-induced broadening of the 21.5 MHz hyperfine transition. (b) The corresponding linewidth is plotted as a function of the applied RF power. A power broadening trend is present, however, the behavior differs from the expected square root dependence. All measurements were performed in pointwise mode and at a temperature of 4.2 K.

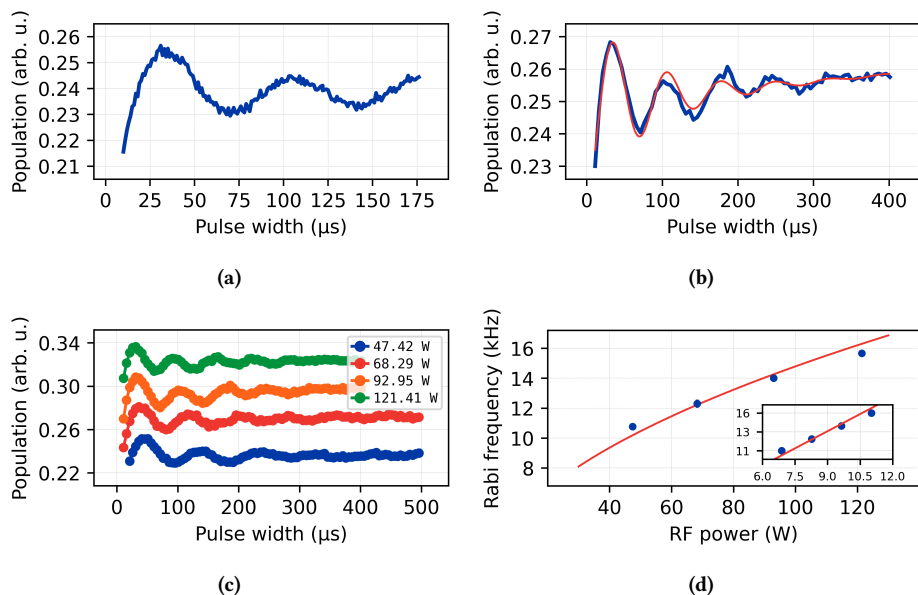


Figure 4.28: Rabi oscillation measurements of the 21.5 MHz hyperfine transition of SKR520. (a) A representative Rabi oscillation measurement using a small step size of $1\ \mu\text{s}$ demonstrates clear oscillatory behavior and enables an accurate determination of the Rabi frequency. (b) Full Rabi measurement over a longer timescale showing multiple oscillations. The data are fitted with a damped sinusoidal function, yielding a Rabi frequency of $(14.01 \pm 0.15)\ \text{kHz}$, while the background contribution is corrected by a saturation function. (c) Power dependence of the Rabi oscillations at different RF powers, shown in the legend. As expected, higher driving powers lead to an increase of the Rabi frequency. For improved visualization, the individual curves are vertically offset by constant values. (d) Rabi frequency plotted as a function of the applied RF power, exhibiting the expected square root dependence. In the inset, the Rabi frequency is shown as a function of the square root of the RF power. A linear fit (red line) results in a proportionality factor of $1.48\ \text{kHz}/\sqrt{W}$. All measurements were carried out at a temperature of $4.2\ \text{K}$.

sured linewidth is about $(154 \pm 16)\ \text{kHz}$. The undesired side effect is that the signal contrast strongly decreased at low RF powers. In order to reach Rabi frequencies, which are faster than the dephasing rate, we applied high RF power levels and could observe coherent spin oscillations. The pulse sequence used for measuring Rabi oscillations differs from that of the ODNMR scheme only in the RF pulse. An RF pulse with a predefined step size between 1 and $25\ \mu\text{s}$ was applied at the center of the spin inhomogeneous line, and each measurement point was averaged over five repetitions before proceeding to the next. The resolution of the measurement is determined by the step size, however, for example, with a step size of $1\ \mu\text{s}$, the total measurement time was approximately $13\ \text{h}$. Therefore, the measurement shown in Figure 4.28(a) was restricted to a limited RF pulse duration of $175\ \mu\text{s}$, but the result clearly demonstrates the observation of Rabi oscillations, with a frequency of approximately $(14.01 \pm 0.15)\ \text{kHz}$. Figure 4.28(b) depicts

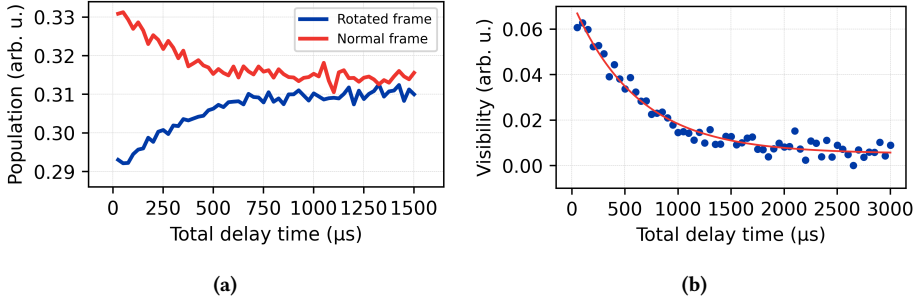


Figure 4.29: Spin echo measurements of the 21.5 MHz hyperfine transition of SKR520.

(a) Time evolution of the two spin-state signals. The final $\pi/2$ pulse is phase-shifted by 180° in one of the measurements to improve the contrast. The resulting *visibility* reflects the population difference between the two spin states normalized to their sum. (b) Measurement of an RF-induced spin echo using a Hahn echo sequence, while preparation and readout are performed in the optical domain. The visibility shown in the spin echo measurement is derived from the two-state readout presented in (a). Its decay as a function of the total delay time between the $\pi/2$ and π pulses provides access to the intrinsic spin coherence time $T_{2,s}$, which was extracted to be $(613 \pm 36) \mu\text{s}$ from an exponential fit. Both measurements were performed at a temperature of 4.2 K.

an extended Rabi measurement using a step size of $5 \mu\text{s}$ for the pulse duration, optical ($\sim 4.5 \text{ mW}$) and RF power ($\sim 92.95 \text{ W}$) were maintained at the same values as in the measurement in Figure 4.28(a). The resulting data were fitted using a damped sinusoidal function. In addition, the Rabi signal possesses a background contribution, which likely originates from thermal effects induced by the RF coil. A comparable linear background contribution in optical Rabi oscillations has also been reported by Ulanowski *et al.* [124]. The background could be fitted using a linear model, or in this case, a saturation function of the form $S(x) \propto (c \cdot x + e)/(g + x)$. Nonetheless, a power series, which is shown in Figure 4.28(c), confirmed the expected behavior: increasing the RF power led to higher Rabi frequencies, consistent with theoretical predictions. As illustrated in Figure 4.28(d), the power dependence of the Rabi frequency was analyzed, and the resulting fit yielded a proportionality factor of $1.48 \text{ kHz}/\sqrt{W}$ characterizing the scaling behavior.

The spin echo coherence time was then determined using an RF-induced Hahn echo measurement. This sequence is the same as the one used for photon echoes in the optical domain and was adapted accordingly. The $\pi/2$ and π pulse durations were extracted from the prior Rabi measurement at an RF power of 92.95 W , resulting in an $18 \mu\text{s}$ $\pi/2$ and $36 \mu\text{s}$ π pulse. To extract a first estimate of the spin coherence time, the echo amplitude, corresponding to the spin population, was measured as a function of the total delay time between $\pi/2$ and π pulses. In order to improve the contrast, the signal is read out sequentially from two spin states. For one measurement, the final $\pi/2$ pulse is rotated by 180° with respect to the initial one, while in the other measurement no rotation was performed. This enabled the observation of symmetric redistribution of spin populations toward thermal equilibrium, as illustrated in Figure 4.29(a). From this,

4. Ensemble spectroscopy of Eu^{3+} -based molecular complexes

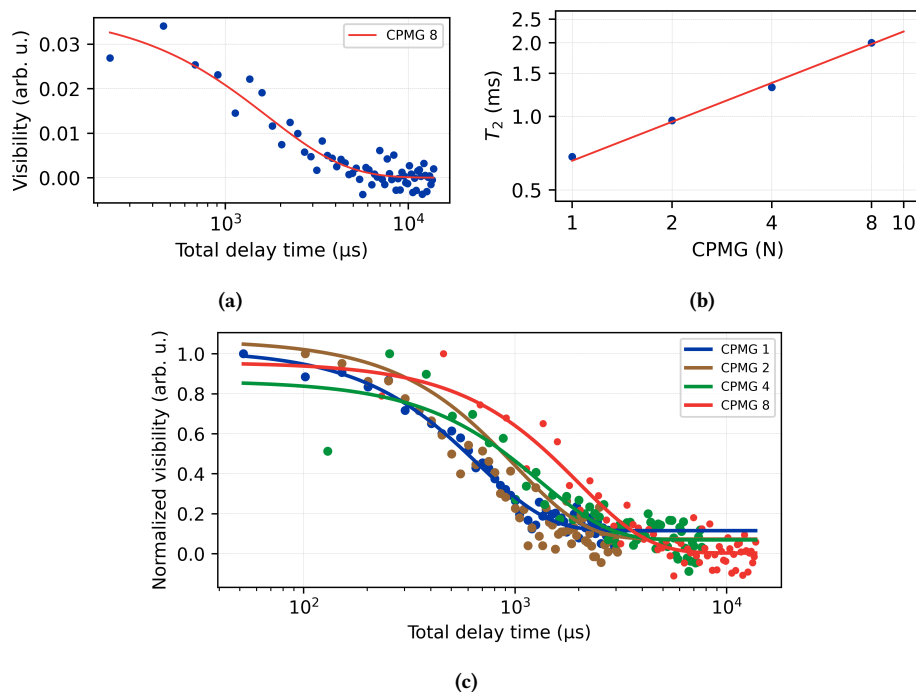


Figure 4.30: Spin echo measurements using dynamical decoupling control sequences. (a) Visibility decay as a function of total delay time for a representative CPMG measurement applying eight refocusing pulses, yielding a spin coherence time $T_{2,s(\text{CPMG})}$ of (2.0 ± 0.2) ms. (b) Scaling law of the spin coherence time $T_{2,s(\text{CPMG})}$ as a function of the number N of refocusing pulses. The data demonstrate the expected trend of $T_2 \propto N^\beta$, where β denotes the scaling exponent. A linear fit on a double logarithmic scale reveals a scaling factor of (0.53 ± 0.03) , indicating decoherence induced by the surrounding spin bath. (c) Summary of all CPMG measurements for 1, 2, 4, and 8 refocusing π pulses, plotted together for direct comparison. The visibility is normalized to the maximum of each measurement and then fitted with a stretched exponential function $\propto e^{-(t/T_2)^\xi}$, using the same stretching factor of 1.31 for every data set (average value from all measurements: 1.43, 1.18, 1.32, 1.31, respectively, for 1, 2, 4, and 8 π pulses). All measurements were performed at a temperature of 4.2 K.

the *visibility*, defined as the difference between the populations of the two spin states normalized to their sum, was introduced. The decay of the visibility over the total delay time was then fitted with an exponential function, yielding an intrinsic spin coherence time $T_{2,s}$ of (613 ± 36) μs for this molecular complex. Figure 4.29(b) depicts the resulting echo decay derived from the readout of the two spin states shown in Figure 4.29(a). With this, the fundamental spin properties of the SKR520 molecular compound have been established.

The next logical step involves applying dynamical decoupling sequences to protect the probed spin ensemble from decoherence caused by the surrounding spin bath, primarily due to the hydrogen nuclear spins in the ligand field or additional spin impurities (potentially from host spin or paramagnetic spins from other REI species). Such protection is expected to significantly increase the spin coherence times. We focused on the fastest and most straightforward approach: the CPMG dynamical decoupling sequence. For this, we again modified our pulse sequence. In CPMG, the π pulse must be applied along a different axis than the $\pi/2$ pulses, for example, $\pi/2$ about x and π about y to suppress the accumulation of phase errors. Figure 4.30(a) shows a representative CPMG measurement for $N = 8$ refocusing π pulses. The measurements with $N = 1, 2, 4$, and 8 refocusing pulses followed the expected trend and scaled according to [125, 126, 127]:

$$T_{2,s(\text{CPMG})} = T_{2,s(\text{echo})} \cdot N^{\beta}, \quad (4.3.3)$$

where β denotes the scaling factor and $T_{2,s(\text{echo})}$ the spin coherence time obtained from spin echo measurements. All spin echoes from the CPMG measurements are summarized in Figure 4.30(c), with the longest observed nuclear spin coherence time $T_{2,s(\text{CPMG})}$ in our measurements of (2.0 ± 0.2) ms. Each individual decay was normalized to its respective maximum and then fitted using a stretched exponential function $\propto e^{-(t/T_2)^{\xi}}$, where ξ denotes the stretching factor. For the summary plot, the averaged stretching factor of 1.31 (average value from all measurements: 1.43, 1.18, 1.32, 1.31, respectively for 1, 2, 4, and 8 π pulses) was utilized. The measurements follow the CPMG scaling law, as depicted in Figure 4.30(b), yielding a scaling exponent of (0.53 ± 0.03) . The extracted scaling factor is relatively close to $\beta = 2/3$, indicating that the dominant source of dephasing is a surrounding single nuclear spin bath [126, 127]. As discussed, this is most likely due to proton spins of the hydrogen atoms. Future steps include the implementation of sequences, such as XY or Knill composite pulses, and the use of an external magnetic field to investigate spin-locking techniques on the spin bath of the ligand fields.

Two additional final measurements were performed. First, a spin hole burning experiment was carried out, analogous to the optical domain. A π pulse was used to burn a spin hole into the spin inhomogeneous line, which was subsequently probed point-by-point with a second RF pulse. The obtained spin holes are shown in Figure 4.31(a) and (b) for two different RF powers, 92.95 W and 47.42 W, respectively, indicating that power broadening effects also occur here. The extracted linewidth provides a first estimate of the pure spin dephasing time $T_{2,s}^*$. For our second line, with a measured width of (11.64 ± 0.60) kHz, this corresponds to a dephasing time of $T_{2,s}^* = (27.3 \pm 1.4)$ μs . A Ramsey sequence would be an alternative method to probe this.

The second measurement studies the correlation between the optical and spin inhomogeneous linewidths. Prior work by Yamaguchi *et al.* on Eu^{3+} doped into Y_2O_3 [49, 128] has shown that detuning from the center of the optical inhomogeneous line results in variations in the spin linewidth, with a reported slope factor of about 10 kHz GHz^{-1} . Figure 4.32 demonstrates this effect, yielding an average rate of approximately 18 kHz of spin-linewidth broadening per gigahertz of optical detuning toward the wings of the optical inhomogeneous line. Identifying and understanding such correlations or

4. Ensemble spectroscopy of Eu^{3+} -based molecular complexes

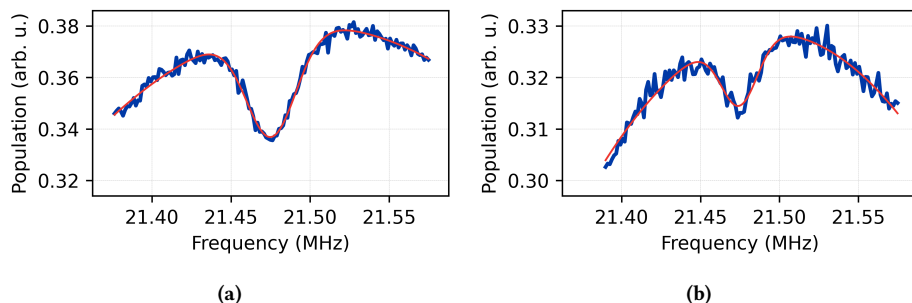


Figure 4.31: Spin hole burning measurements of the 21.5 MHz hyperfine transition of SKR520. (a) and (b) show two representative spin hole burning measurements, where narrow Gaussian-shaped holes are burned within the broader inhomogeneous Lorentzian distribution of the 21.5 MHz hyperfine transition. A Gaussian fit (red curves) was applied to each central feature to extract the linewidth of a spin subclass, yielding (15.70 ± 0.32) kHz (RF power of ~ 92.95 W) and (11.64 ± 0.60) kHz (RF power of ~ 47.42 W), respectively. The trend of power broadening is clearly observed across these measurements, analogous to similar effects in the optical domain, indicating the impact of excitation power on the transition linewidth. Both measurements were performed at a temperature of 4.2 K.

effects induced by the local environment is crucial for evaluating the suitability of new molecular materials for future quantum technologies.

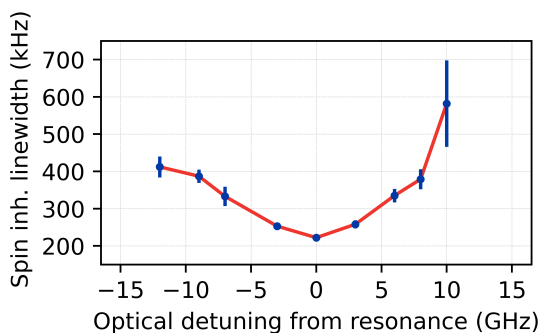


Figure 4.32: Correlation between optical and spin inhomogeneous lines of SKR520. Correlation between the optical and spin inhomogeneous linewidths measured across different spectral positions of the optical transition but on the same 21.5 MHz hyperfine transition. The data reveal a slope factor in both directions, indicating that ions detuned from the optical center experience broadened spin transitions. An average scaling factor of approximately 18 kHz of spin-linewidth broadening per gigahertz of optical detuning toward the wings of the optical inhomogeneous line is extracted from the data, excluding the data point with the highest uncertainty. All measurements were performed in pointwise mode and at a temperature of 4.2 K.

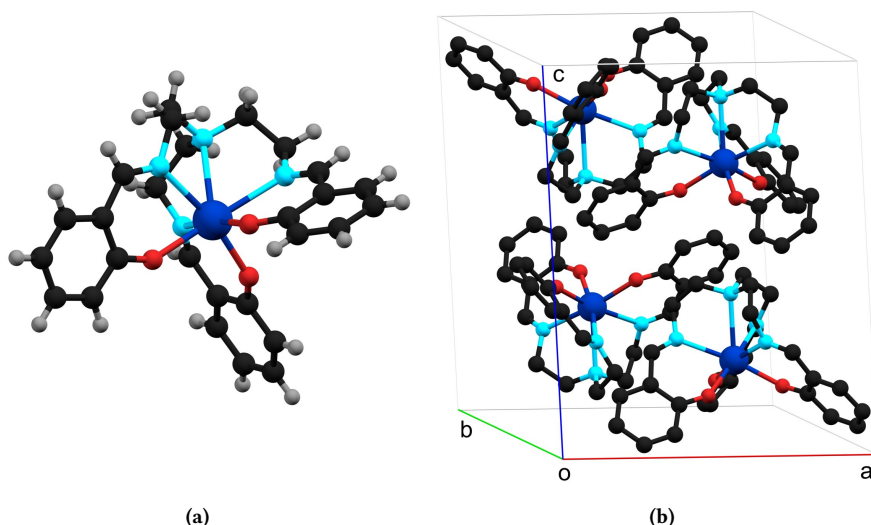


Figure 4.33: Crystal structure of [Eu(trensal)]. (a) X-ray crystal structure of a single [Eu(trensal)] molecular complex. Europium is shown in blue, oxygen in red, nitrogen in cyan, carbon in black, and hydrogen in gray. (b) The unit cell contains four molecules with different orientations in the trigonal crystal structure. The hydrogen atoms are omitted for clarity.

4.3.2. Analysis of the molecular complex [Eu(trensal)]

In this study, we focused on the prototypical charge-neutral mononuclear Eu^{3+} complex [Eu(trensal)], with trensal referring to 2,2',2''-tris(salicylideneimino)-triethylamine. The results presented here are based on and further extend the findings published in our recent work [37]. The selection of [Eu(trensal)] in this study is motivated by earlier investigations of its structurally analogous system, [Yb(trensal)], where Pedersen *et al.* demonstrated coherent spin control using pulsed electron paramagnetic resonance spectroscopy on single crystals. In that study, the Yb^{3+} ion ($S = 1/2$, $I = 5/2$) exhibited pronounced Rabi oscillations, with coherence maintained over more than 70 rotations, highlighting the suitability of a trensal-coordinated REI-based molecular complex for implementing coherent spin control [129]. [Eu(trensal)], which we will refer to from now on as **SKR127**, was synthesized according to the procedures reported in Ref. [129]. Single-crystal X-ray diffraction confirmed that the complex crystallizes in the trigonal system with space group $P\bar{3}c1$. The Eu^{3+} ion is coordinated in a C_{3v} -symmetric ligand environment, and the coordination geometry is best described as a capped octahedron. The molecular geometry and crystal packing of the SKR127 complex are illustrated in Figure 4.33, displaying in (a) the capped octahedral coordination around the Eu^{3+} center and in (b) the arrangement of the four molecules within the trigonal unit cell.

This mononuclear molecular complex exhibits a powder-like morphology composed of pencil-shaped microcrystals. For ensemble spectroscopy, the sample was integrated

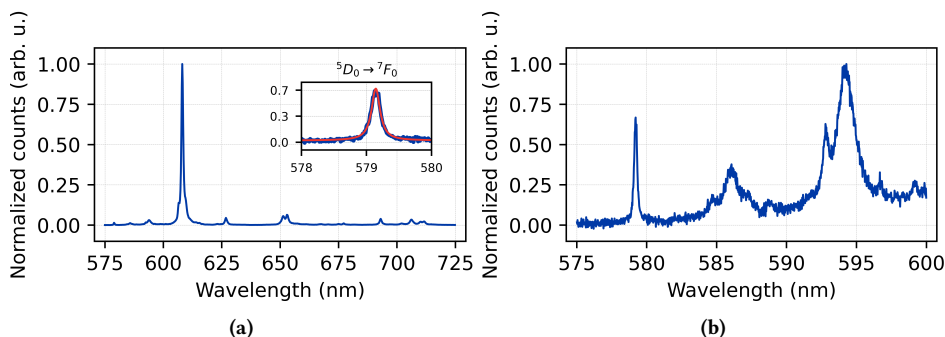


Figure 4.34: Photoluminescence spectra of SKR127. (a) Room-temperature emission spectrum showing all resolved $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions up to $J = 4$. The inset represents a fit to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition centered around 579.214 nm. (b) Zoomed-in view of the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition region. The intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ compared to SKR520 indicates a higher branching ratio, as the intensity difference relative to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is smaller. Both spectra are normalized to their respective maximum intensities.

into our fiber-based ferrule sample holder, and the measurements were performed at 4.2 K using the exchange gas dipstick.

Room-temperature PL spectra, as depicted in Figure 4.34(a) and (b), reveal the characteristic emission lines, including the coherent $^5\text{D}_0 \rightarrow ^7\text{F}_0$ at 579.214 nm with a width of (0.223 ± 0.002) nm, accompanied by the expected $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions. In comparison to SKR520, the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ line exhibits a significantly higher intensity relative to the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, which is insensitive to the ligand field, indicating a potentially higher branching ratio. This improvement in optical characteristics is generally favorable for efficient optically addressable molecular systems. Using off-resonant pulsed excitation with 532 nm, the excited-state lifetime was determined to be (336.99 ± 0.23) μs , as shown in Figure 4.35(a). This value sets a natural lifetime-limited linewidth of approximately 450 Hz. In addition, the molecular complex was observed to be very photostable throughout all measurements.

In order to investigate the inhomogeneous broadening, multiple PLE scans were performed at cryogenic temperatures. The resulting spectrum, presented in Figure 4.35(b), shows a Lorentzian line shape centered at 579.45 nm, corresponding to 517 374 GHz, with a FWHM linewidth of approximately 91 GHz. Due to the limited scanning range of our dye laser, the whole spectrum was acquired in several scans, which were then stitched together for the evaluation. So far, this is the broadest line we have observed within our studies. However, a broad inhomogeneous linewidth does not necessarily correspond to a broad homogeneous linewidth.

The homogeneous linewidth was measured via the SHB technique. The applied pulse sequence consisted of a 500 ms burn pulse, a 350 ms probe pulse, and an erasing sequence composed of 200 pulses, each lasting 20 ms, with 2 ms delay time between them. Each

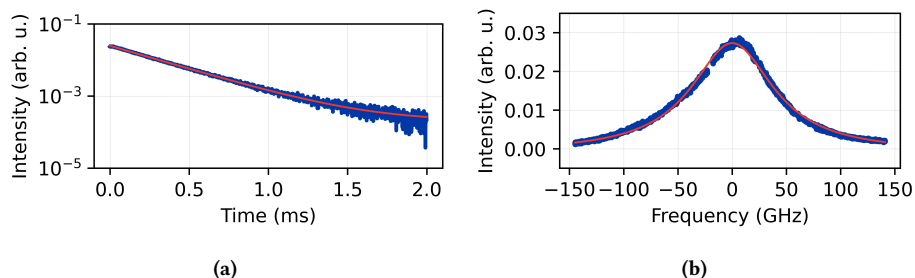


Figure 4.35: Excited-state lifetime and inhomogeneous linewidth of SKR127. (a) Measured excited-state lifetime $T_{1,0}$ of the molecular complex SKR127 at room temperature, fitted with a monoexponential function yielding a value of $(336.99 \pm 0.23) \mu\text{s}$. (b) Stitched inhomogeneous line scan over five measurements for the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. The PLE scan reveals a broad inhomogeneous profile with a width of (91.0 ± 0.4) GHz recorded at 4.2 K, while no corresponding broad homogeneous linewidth was observed in subsequent SHB measurements.

SHB scan was averaged over 100 repetitions and background corrected prior to fitting. The narrowest spectral hole measured, as shown in Figure 4.36(a), yielded a hole width of (5.6 ± 0.2) MHz. A maximum hole contrast of about 50 % was achieved under optimized excitation parameters, demonstrating effective population redistribution among other hyperfine levels. The complex is not isotopically purified, so signal contributions from both isotopes are expected. Besides the central hole, initial side features are slightly resolved, including anti-holes at approximately ± 14.4 , 20.4, and 36.4 MHz, and side holes around ± 43.4 MHz. These features hint at the underlying hyperfine structure. However, new high-resolution measurements over the whole SHB spectrum with improved

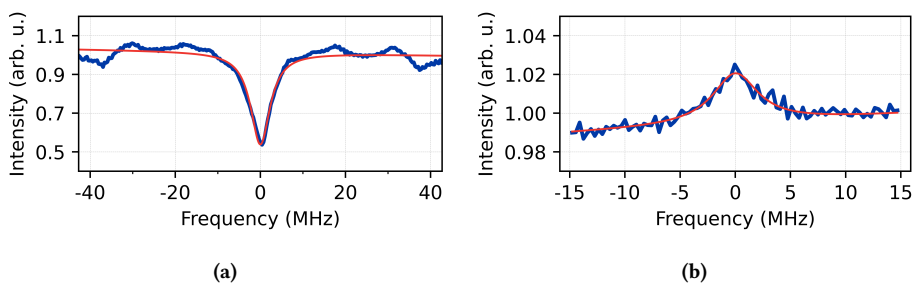


Figure 4.36: SHB measurements of SKR127. (a) Fluorescence-detected spectral hole showing a width of (5.6 ± 0.2) MHz, fitted with a Lorentzian profile (both (a) and (b) in red). Besides the central hole, first slightly resolved side features including anti-holes (e.g., ± 14.4 , 20.4, and 36.4 MHz) and side holes (e.g., ± 43.4 MHz) can be identified. However, for an extraction of the hyperfine splittings, additional SHB spectra with high-quality resolution are required to perform a fit to the data. (b) Corresponding transmission-detected SHB spectrum, revealing a hole width of (5.6 ± 0.8) MHz with lower contrast potentially due to a lower optical depth of the prepared sample. Both measurements were performed at a temperature of 4.2 K.

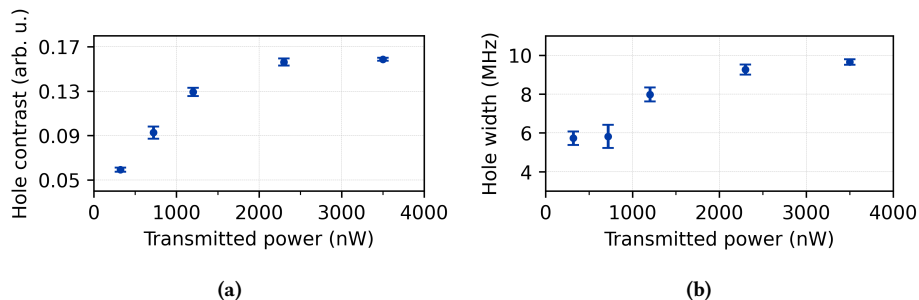


Figure 4.37: Laser power dependencies of the homogeneous linewidth of SKR127. (a) Spectral hole contrast and (b) hole width as a function of the excitation power obtained from SHB measurements. The hole width increases with power, indicating power broadening, while the contrast improves up to a saturation point. These trends are required for the selection of optimal pulse parameters in order to achieve potentially high-quality SHB measurements, preventing possible broadening effects. Both measurements were performed at a temperature of 4.2 K.

signal quality are needed to extract reliable hyperfine splittings via fitting procedures. Furthermore, an SHB measurement could be performed by detecting the absorption signal, which is achieved without filtering the transmitted light through the sample, as represented in Figure 4.36(b). This method yielded a weaker signal with about 2 % hole contrast and a spectral hole width of (5.6 ± 0.8) MHz, consistent with the fluorescence-based SHB results. Lower excitation power produced comparable hole widths, indicating that the measurements were not limited by power broadening. It is noted that the contrast of the spectral hole may be further improved by increasing the optical depth through our new and optimized sample preparation method.

In order to investigate broadening mechanisms induced by the driving laser power, the SHB pulse sequence was applied while varying the laser power incident on the sample. Figure 4.37(a) and (b) show the dependence of the spectral hole contrast and linewidth on the laser power. In this measurement, the maximum contrast was approximately 16 %, more than a factor of three lower than in the earlier data presented in Figure 4.36(a), which was observed under optimized conditions in a previous measurement series. The reduced signal contrast is attributed to slight differences in optical depth between the two cooldowns arising from variations during the sample preparation. However, the transmitted laser power was limited to approximately $1 \mu\text{W}$ due to strong scattering within the powder-like sample. Both the hole contrast and linewidth were observed to increase with laser power, as expected from power broadening. At transmitted powers below $1 \mu\text{W}$, the SNR degraded significantly, limiting further spectral hole-width measurements. This may suggest that even narrower homogeneous linewidths could be observed, especially when using sensitive techniques like photon echoes. Unfortunately, under these conditions, no echo signals could be detected, likely due to the insufficient optical depth of the prepared SKR127 sample.

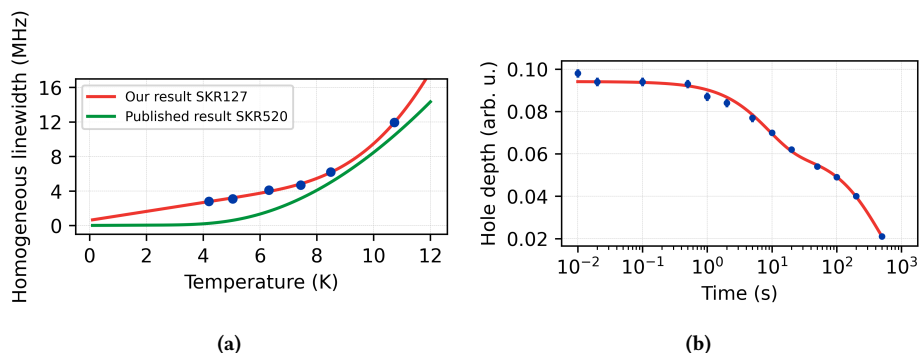


Figure 4.38: Temperature-dependent optical dephasing and hyperfine lifetime of SKR127. (a) Homogeneous linewidth Γ_h as a function of temperature up to about 10 K (blue dots), obtained via SHB measurements. The fitted data (red curve) reveals a linear increase at low temperatures up to about 8 K, indicative of coupling to TLSs, followed by a steeper exponential rise at temperatures above this threshold, attributed to phonon-mediated dephasing via coupling with quasi-localized vibrational LFM. Compared to the reported results (green curve) in Ref. [1], the onset of this exponential behavior appears at slightly elevated temperatures, and the increase in linewidth is potentially more pronounced, suggesting stronger phonon-mediated dephasing mechanisms in the molecular system SKR127. (b) Spectral hole depth decay measured at a temperature of 4.2 K, fitted with a double-exponential decay and thus yielding two relaxation components: a short time constant of $T_{1,s(\text{short})} = (7 \pm 1) \text{ s}$ and a long time constant of $T_{1,s(\text{long})} = (460 \pm 80) \text{ s}$. This constitutes the longest nuclear spin lifetime observed in this study, highlighting the potential of this complex for long-lived spin storage experiments.

The next measurement focused on the temperature-dependent behavior of the homogeneous linewidth of SKR127, following a similar procedure as described in the previous section. The evolution of the homogeneous linewidth as a function of temperature up to 10 K exhibited a similar characteristic trend to that observed in SKR520, as shown in Figure 4.38(a). This confirms that the temperature-dependent broadening in this temperature regime can be well described by the model introduced in Ref. [61], which accounts for interactions with TLSs and quasi-localized vibrational LFMs. A fit to the data using the expression from Equation 4.3.1 yielded the parameters $\Gamma_0 = 0.605 \text{ MHz}$, $\alpha_{\text{TLS}} = 514 \text{ kHz K}^{-1}$, $\alpha_{\text{LFM}} = 2388 \text{ MHz}$ (with high uncertainty) and $\Delta E_{\text{LFM}} = 1347 \text{ GHz}$. It is important to note that the extracted fit parameters, particularly those related to the contribution of LFMs, possess significant uncertainties and should be validated through repeated measurements to ensure their correctness and reproducibility. In comparison with SKR520, the exponential increase attributed to phonon-mediated dephasing due to LFMs sets in at a higher temperature, at around 8 K, rather than 3.5 K. This shift to a higher temperature and steeper increase suggests material-specific differences in vibrational coupling mechanisms. Overall, this result underlines that molecular complexes can be reliably modeled in the low-temperature regime and are indeed sensitive to similar dephasing mechanisms as observed in REI-based solid-state systems.

In the final step, the hyperfine lifetime $T_{1,s}$ was investigated by varying the time delay between the burn and the probe pulses in the SHB sequence. The decay of the spectral hole depth over time was fitted using a double-exponential function, as represented in Figure 4.38(b), yielding two decay times $T_{1,s(\text{short})} = (7 \pm 1) \text{ s}$ and $T_{1,s(\text{long})} = (460 \pm 80) \text{ s}$, which were already observed in other molecular and solid-state materials [1, 67]. These results demonstrate the longest hyperfine lifetimes among our investigated molecular compounds, confirming the suitability of SKR127 for potential quantum memory experiments, as soon as additional nuclear spin coherence measurements are successfully demonstrated.

4.3.3. Analysis of the molecular complex $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$

The molecule $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ is an isostructural charge-neutral complex which consists of an Eu^{3+} ion coordinated by the tetradentate functional phen-based ligand system known as 2,9-bis(pyrazol-1-yl)-1,10-phenanthroline (dpphen) [130] and three nitrate (NO_3) ligands. The planar representation of this molecular compound is depicted in Figure 4.39(a). Single-crystal X-ray diffraction analysis revealed the presence of two distinct structural polymorphs of the complex: a puckered configuration referred to as $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ -puck, and a nearly planar configuration referred to as $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ -plan, as shown in Figure 4.39(b) and (c) [108].

In both molecular structures, the Eu^{3+} ion exhibits a coordination number of ten, with the ligand arrangement leading to a C_{2v} point group symmetry around the ion center. In the puckered form, the pyrazole rings of the dpphen ligand are rotated out of the plane defined by the phenanthroline core, resulting in a more distorted coordination geometry. The variant $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ -puck crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. In contrast, the $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ -plan configuration shows reduced distortion and crystallizes in a monoclinic space group $P2_1/c$ with four molecules per unit cell. In this case, the puckering is less pronounced, resulting in a close-to-planar configuration of the dpphen ligand around the Eu^{3+} ion.

A continuous shape measure analysis was performed in order to determine the exact coordination symmetry around the Eu^{3+} center. For the puckered structure, the coordination environment is best described as sphenocorona, while the planar form represents a tetradecahedron, with both retaining C_{2v} symmetry. Despite their structural differences, powder X-ray diffraction studies indicate that the bulk material or large amounts of compressed powder are predominantly composed of the puckered form, with the planar polymorph contributing only minimally. For this reason, only a single inhomogeneous linewidth is expected, whereas in our previous investigations on molecular systems containing comparable amounts of both polymorphs, a double peak in the inhomogeneous line was observed [62]. In general, this low-symmetry coordination environment is favorable for REI-based optical transitions. For simplicity, the molecular complex $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ is hereafter referred to as **SKR147**.

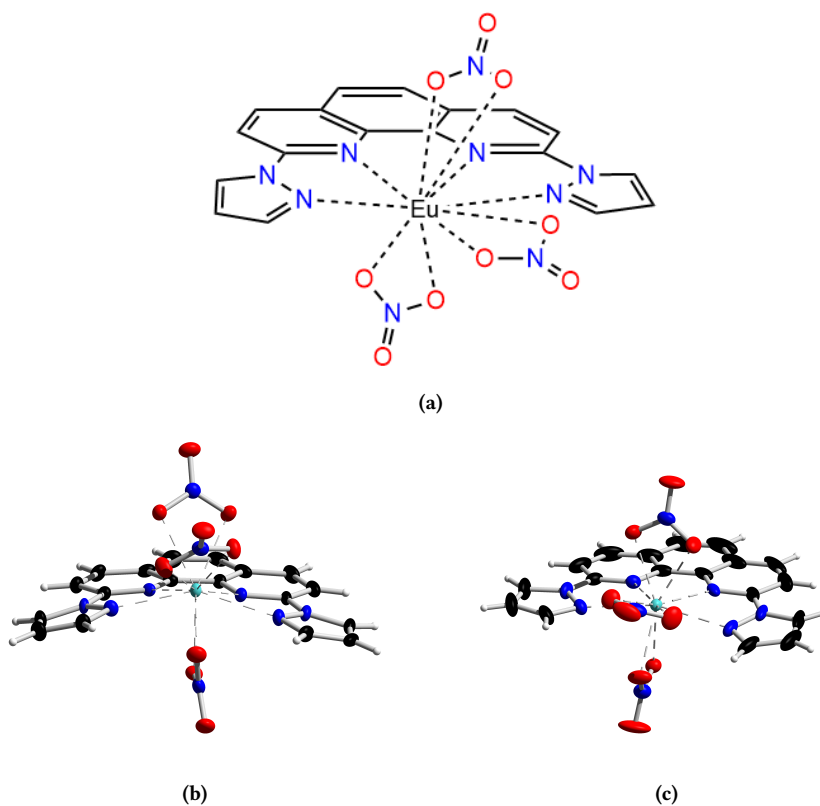


Figure 4.39: Molecular structure of $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$. (a) Planar representation of the mononuclear $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ molecular compound. (b) and (c) represent X-ray crystal structures of the two polymorphs $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ -puck and $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$ -plan, respectively. Europium is shown in cyan, oxygen in red, nitrogen in blue, carbon in black, and hydrogen in white. All three figures were provided by our collaborator **Dr. Sören Schlittenhardt**.

The room-temperature emission spectrum of SKR147 features the expected $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions, with the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition observed at 580.527 nm and exhibits a linewidth of (0.279 ± 0.008) nm, as seen in Figure 4.40(a). Its relatively low branching ratio of 0.11 % is consistent with the parity-forbidden nature of this transition. However, the observation of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition confirms the presence of a low-symmetry C_{2v} coordination environment, which is a requirement for partially allowed transitions. In addition, a detailed examination of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, which is illustrated in Figure 4.40(b), was performed by Schlittenhardt *et al.* [108], revealing six emission lines instead of three. This indicates the contribution of both polymorphs in the crystal lattice. Each contributes three peaks due to the full lifting of the degeneracy by the C_{2v} symmetry. These findings are in good agreement with the structural analysis confirming the two forms: the dominant puckered and the minor planar polymorph.

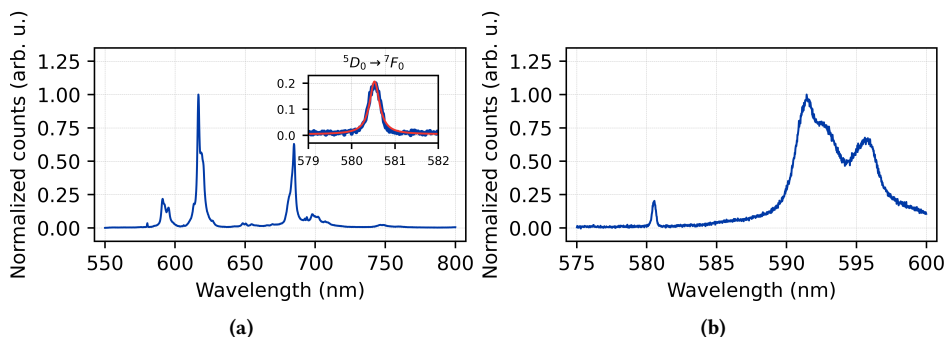


Figure 4.40: Photoluminescence spectra of SKR147. (a) Room-temperature emission spectrum showing the set of resolved $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions up to $J = 5$. The inset represents a fit to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition centered around 580.527 nm. (b) Zoomed-in view of the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition region, revealing a relatively low branching ratio for the coherent $^5\text{D}_0 \rightarrow ^7\text{F}_0$. Both spectra are normalized to their respective maximum intensities.

Off-resonant pulsed excitation at 532 nm yielded an excited-state lifetime of $T_{1,0} = (1.437 \pm 0.001)$ ms of SKR147, as illustrated in Figure 4.41(a). To perform ensemble spectroscopy at 4.2 K, the crystalline powder of SKR147 was prepared in our fiber-based ferrule sample holder and was cooled using the exchange gas dipstick. Figure 4.41(b) illustrates the PLE scan revealing a peak at 580.908 nm, corresponding to 516 075.36 GHz, and an inhomogeneous linewidth of (16.44 ± 0.03) GHz. The narrow inhomogeneous linewidth indicates a high crystalline order in the powder-like sample. As expected, only a single line was resolved in the PLE scan, attributed to the dominant contribution of the puckered polymorph.

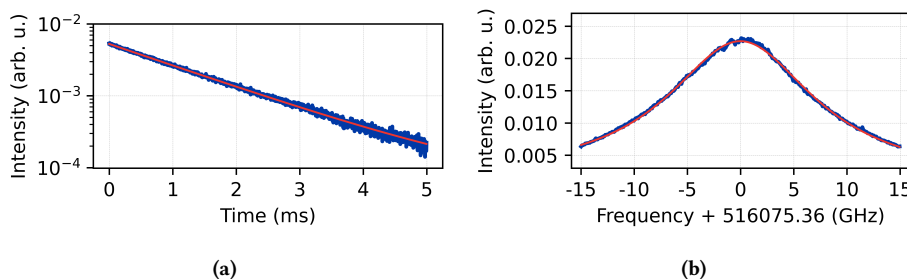


Figure 4.41: Excited-state lifetime and inhomogeneous linewidth of SKR147. (a) Room-temperature fluorescence decay of SKR147 measured at the $^5\text{D}_0 \rightarrow ^7\text{F}_{J \geq 2}$ transitions. The data is fitted with a monoexponential function yielding an excited-state lifetime $T_{1,0}$ of (1.437 ± 0.001) ms. (b) PLE scan of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition recorded at 4.2 K. The fit to the Lorentzian line shape of the inhomogeneous broadening reveals a linewidth of (16.44 ± 0.33) GHz.

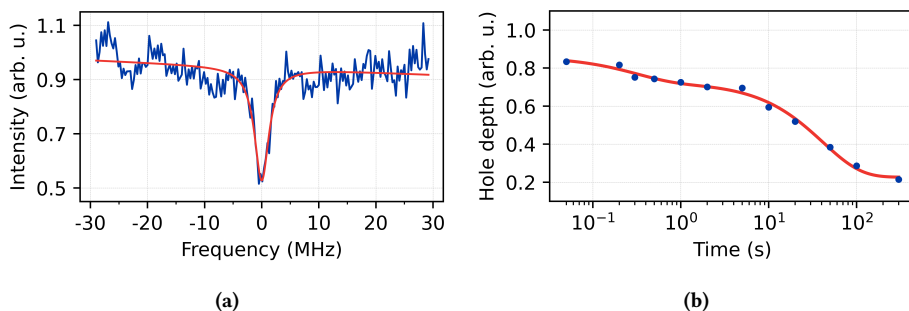


Figure 4.42: SHB and hyperfine lifetime of SKR147. (a) SHB measurement performed by applying a 500 ms burn and 200 ms probe pulse. The recorded spectral hole is fitted with a Lorentzian function, resulting in a hole width of (3.10 ± 0.31) MHz and a hole contrast of approximately 40 %. (b) Decay of the spectral hole depth as a function of the delay time between burn and probe pulses, used to extract the hyperfine spin lifetime. A double-exponential fit reveals two hyperfine spin relaxation components: a fast time constant with $T_{1,s(\text{short})} = (0.31 \pm 0.14)$ s and a slower one with $T_{1,s(\text{long})} = (41.29 \pm 5.29)$ s. Both measurements were performed at a temperature of 4.2 K.

In order to gain some insights into the optical coherence properties, SHB measurements were carried out. A 500 ms burn pulse followed by a 200 ms probe pulse scanned over 60 MHz yielded a spectral hole with a width of (3.10 ± 0.31) MHz, which is shown in Figure 4.42(a). This corresponds to a homogeneous linewidth of (1.55 ± 0.16) MHz and thus a $T_{2,o}^* = (205 \pm 21)$ ns.

The relaxation of the hole depth over time was used to evaluate the nuclear spin lifetime in the ground state levels. A double-exponential fit to the spectral hole depth yielded two distinct lifetimes $T_{1,s(\text{short})} = (0.31 \pm 0.14)$ s and $T_{1,s(\text{long})} = (41.29 \pm 5.29)$ s, as represented in Figure 4.42(b). These results are in line with our previous findings on Eu^{3+} -based molecular systems.

4.3.4. Analysis of the molecular complex $[\text{Eu}(\text{btfa})_3(\text{bipy})]$

In this subsection, we investigate the mononuclear Eu^{3+} β -diketonate complex $[\text{Eu}(\text{btfa})_3(\text{bipy})]$, as illustrated in Figure 4.43(a) and (b). Here, the Eu^{3+} ion is coordinated by three btfa ligands (4,4,4-trifluoro-1-phenyl-1,3-butanedione), forming the backbone of the molecular structure via oxygen atoms and an auxiliary ligand, bipy (2,2'-bipyridine), which coordinates neutrally through nitrogen atoms. The complex crystallizes in the monoclinic space group $P2_1/n$, with four molecules per unit cell. The Eu^{3+} ion adopts an eight-coordinate environment that exhibits an approximate square antiprismatic geometry [131], corresponding to a point group symmetry of D_{4d} [132]. The synthesis and structural characterization of the $[\text{Eu}(\text{btfa})_3(\text{bipy})]$ molecular complex

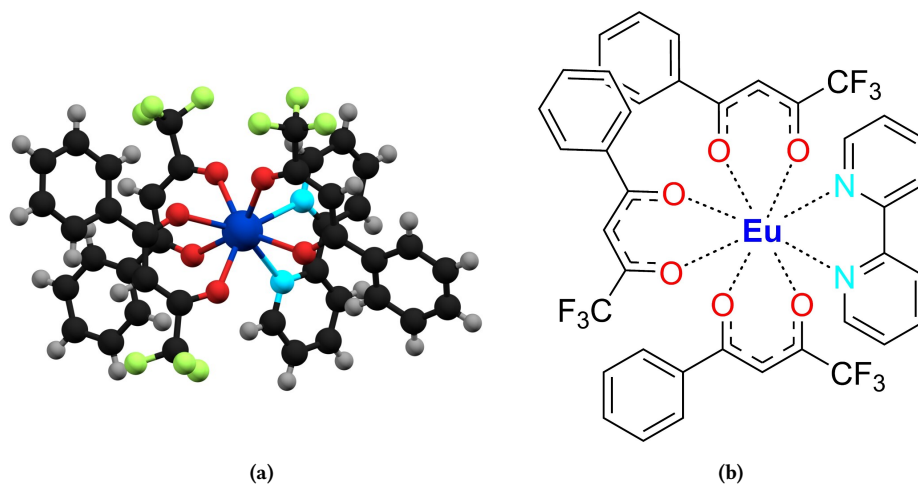


Figure 4.43: Molecular structure of [Eu(btfa)₃(bipy)]. (a) X-ray crystal structure of a single [Eu(btfa)₃(bipy)] molecular complex. Europium is shown in blue, oxygen in red, nitrogen in cyan, fluorine in green, carbon in black, and hydrogen in gray. (b) Planar representation of the molecular structure. The figure was provided by our collaborator **Dr. Barbora Brachnakova**.

can be found in Ref. [131] and will be detailed in an accompanying publication currently in preparation [132]. For simplicity, this compound is referred to as **BB1** throughout the following discussion.

Additionally, it is important to highlight that, compared to previously discussed molecular compounds, this complex contains fluorinated groups within its β -diketonate ligands. As reported by Batista *et al.* [131], substituting $-\text{CH}_3$ groups with $-\text{CF}_3$ groups enhances luminescence quantum yields by reducing non-radiative decay channels. In Eu^{3+} -based materials, this substitution is particularly beneficial, as it can further increase the quantum yield and potentially give rise to higher branching ratios across several optical transitions, including the inherently weak $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. Theoretical calculations of the molecular structure and electronic energy levels attribute the improved quantum yield to reduced vibronic coupling due to the lower vibrational energies of C–F bonds compared to C–H bonds, optimized donor–acceptor energy differences, and shorter donor–acceptor distances (ligand as donor, Eu^{3+} as acceptor) [131].

Figure 4.44(a) illustrates the room-temperature emission spectrum of BB1, showing the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions up to $J = 4$. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition was typically observed in the wavelength range between 580.11 nm and 580.58 nm, depending on the sample preparation and measurement conditions. Figure 4.44(a) shows an example centered at 580.357 nm, with a linewidth of (0.155 ± 0.009) nm and a relatively low branching ratio of 0.14 %. Figure 4.44(b) depicts a zoomed-in view of the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition region. A double-peak structure is observed

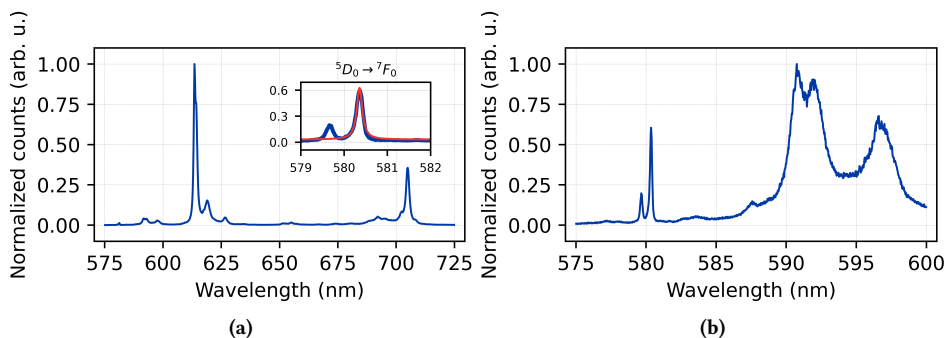


Figure 4.44: Photoluminescence spectra of BB1. (a) Emission spectrum showing all resolved $^5D_0 \rightarrow ^7F_J$ transitions up to $J = 4$ at room temperature. The inset highlights the weak $^5D_0 \rightarrow ^7F_0$ transition at 580.357 nm. (b) Zoomed-in view of the electric dipole $^5D_0 \rightarrow ^7F_0$ and the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition region, revealing a double-peak structure of the coherent transition. The origin of the secondary peak remains unclear and was not considered further. The dominant right peak was used for all subsequent measurements and evaluations. However, the branching ratio remains very low due to the comparatively weak intensity of the coherent transition to the largely environment-independent magnetic dipole transition. Both spectra are normalized to their respective maximum intensities.

for the coherent transition, where the origin of the secondary peak remains unclear and was not considered further. The dominant right peak was used for all subsequent measurements and evaluations, since the second peak did not yield meaningful results. The most interesting aspect is the observation of the $^5D_0 \rightarrow ^7F_0$ transition, as it is theoretically not expected for a D_{4d} site symmetry. However, the peak is visible in the measured PL spectra, suggesting the presence of another low-symmetry site in the coordination environment around the Eu^{3+} ion, which fulfills the requirements for partially allowed transitions.

The ensemble spectroscopy of BB1 was performed in our Sionludi cryostat, reaching temperatures as low as 100 mK. To provide better thermalization to the cold plate of the cryostat, the crystalline powder of BB1 was prepared in a special sample holder design using bare components and a phosphor bronze casing for improved thermal contact. The modified sample holder, which is tightened to the cold plate via a brass screw, was already shown in Section 3.4. Figure 4.45(a) shows the PLE scan resulting in a peak at 580.752 nm, corresponding to 516 214.09 GHz, and an inhomogeneous linewidth of (11.97 ± 0.04) GHz. The scan was performed with a power of 1.1 mW, which was sufficient to provide a good contrast and not excessively warm the cryostat (the temperature increased to 250 mK). The relatively narrow inhomogeneous linewidth of BB1 compared to the other samples may indicate a potentially high crystalline order in the powder form. In addition, the material features strong optical absorption, which allowed the inhomogeneous line to be probed in transmission. However, the corresponding data is not shown here due to redundancy with the fluorescence-based results. The excited-state lifetime was extracted from our SHB measurements. The decay at the end of the burn pulse was fitted with a

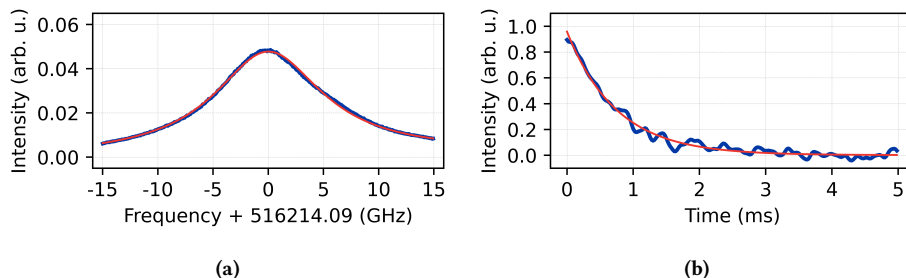


Figure 4.45: Inhomogeneous linewidth and excited-state lifetime of BB1. (a) Inhomogeneous line scan of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition at 100 mK, revealing a Lorentzian line shape (red) centered around $\lambda = 580.752$ nm with a linewidth of (11.97 ± 0.04) GHz. (b) Optical excited-state lifetime $T_{1,o}$ extracted from the decay of the fluorescence signal at the end of the burn pulse in SHB measurements, yielding a value of (747 ± 12) μs . Both measurements were performed at a temperature of 100 mK.

monoexponential function, as illustrated in Figure 4.45(b), resulting in an optical lifetime of $T_{1,o} = (747 \pm 12)$ μs .

In the next step, SHB measurements were performed at 100 mK using our standard pulse sequence of a 500 ms burn pulse, followed by a 200 ms probe pulse and concluded by an erasing sequence. After several power optimization measures, the narrowest spectral hole was burned into the inhomogeneous profile with an optical power of 14 μW , exhibiting a hole width of (1.19 ± 0.08) MHz. This corresponds to a homogeneous linewidth of $\approx (595 \pm 40)$ kHz and hence a $T_{2,o}^* = (535 \pm 36)$ ns. The respective spectral hole is shown in Figure 4.46(a). The measured hole contrast of about 25 % and the narrow linewidth suggest efficient optical pumping in this molecular system at these power levels and low-temperature regime. We believe that even narrower linewidths can be reached through further optimization of the experimental conditions.

Furthermore, the concluding measurement in the Sionludi cryostat involved the temporal evolution of the hole depth as a function of the delay time between burn and probe pulses. In this case, the resulting decay featured only the fast component of the hyperfine lifetime. The data was fitted to a monoexponential function, revealing a relaxation time of $T_{1,s(\text{short})} = (4.25 \pm 0.60)$ s, as represented in Figure 4.46(b). The final SHB measurement was conducted at a delay time of 500 s, showing still a decent hole contrast. This observation suggests an even longer second time component of the hyperfine lifetime, which is not detectable at these low temperatures [67]. In addition, some single SHB measurements were limited due to laser instabilities. Further improvement can be carried out to gain more insights into the hyperfine spin dynamics.

In order to continue our investigations on BB1, we prepared additional samples in the asymmetric fiber configuration of the sample holder, with the intention of inserting more macroscopic crystals from the powder into the larger sample volume. The sample

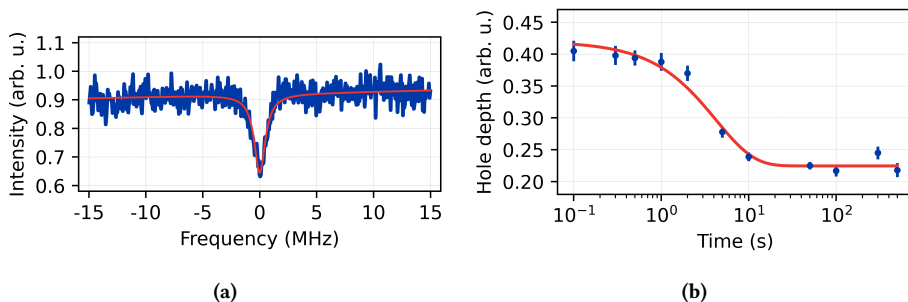


Figure 4.46: SHB and hyperfine lifetime of BB1. (a) Spectral hole recorded using a 500 ms burn and 200 ms probe pulse. The data is fitted to a Lorentzian function, resulting in a hole width of (1.19 ± 0.08) MHz and a hole contrast of approximately 25 %. (b) The decay of the hole depth as a function of the delay time between burn and probe pulses reveals a single exponential relaxation with a fast component of the hyperfine lifetime of $T_{1,s(\text{short})} = (4.25 \pm 0.60)$ s. The second time constant could not be observed, even after a delay time of 500 s, indicating a very long second hyperfine lifetime component. Both measurements were performed at a temperature of 100 mK.

holder was then cooled down to 4.2 K with the flange dipstick cryostat. The initial aim was to perform comparable measurements to those conducted on SKR520, including acquiring the full hole-burning spectrum with resolved side features to later fit it using our simulation model and extract the hyperfine splittings of the ground and excited states. This information is required for future spin characterization attempts. Figure 4.47 presents a first approximation of the excited-state hyperfine energy level structure, showing the right wing of a hole-burning spectrum, with well-resolved side holes and anti-holes. Such a spectrum is achieved via fast probe pulses. The 500 ms burn pulse still needs to be strong to create enough contrast, followed by a short 2 ms probe pulse, which is scanned over a frequency range of 160 MHz. In order to create only one wing of the hole-burning spectrum, the burn pulse is shifted in frequency to either the left or right side of the AOM center frequency, thereby shifting the spectral hole from the center of the spectrum. The fit uses multiple steps, where in the beginning the central hole and then the side holes are fitted. Afterwards, these values are plugged into a transition matrix to identify the ground-state splittings. The side holes correspond to the excited-state splittings of BB1, which, according to the fit, are:

$$ES1 = 43.55 \text{ MHz} \quad \text{and} \quad ES2 = 57.45 \text{ MHz}. \quad (4.3.4)$$

In summary, Figure 4.47 shows a well-converged fit to the spectral region, enabling a first approximation of the excited-state hyperfine structure. However, limitations remain due to the natural isotopic composition of the BB1 molecular complex, where contributions from both Eu^{3+} isotopes result in overlapping features in the hole spectrum and thus no reliable fit can be performed. Although the signal quality has improved compared to earlier measurements, it is still insufficient to resolve weak spectral features attributed to transitions of low oscillator strength. These limitations highlight the need for future

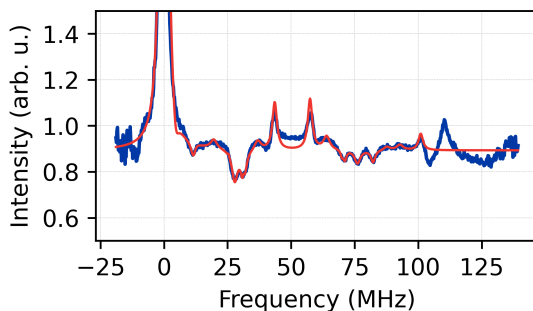


Figure 4.47: Characterization of hyperfine splittings of BB1. Experimental data of the right wing of a hole-burning spectrum, revealing features such as side holes and anti-holes. A fit to the central hole and the side holes yields a determination of the excited-state splittings: $ES1 = 43.55$ MHz and $ES2 = 57.45$ MHz. While the current fit already captures several potential anti-holes, further refinement is required to account for the additional lines arising from the other Eu^{3+} isotope, which disturb the mathematical transition matrix.

measurements on isotopically purified samples, where transitions from a single isotope can be observed, enabling a more accurate and complete hyperfine characterization.

Furthermore, FID and spectral comb measurements concluded the optical characterization of this molecular sample. The FID signal, as shown in Figure 4.48(a), provided a direct estimation of the ensemble dephasing time $T_{2,o,(FID)}^*$ of about (268 ± 2) ns, offering insight into the coherence properties of the system under pulsed excitation. The pulse sequence consists of a $4\text{ }\mu\text{s}$ $\pi/2$ pulse and a subsequent readout pulse at an optical power of 70 mW. Applying a photon echo sequence did not reveal any beating signal, and further measurements for improvement potentially require cooling to millikelvin temperatures. Finally, the successful generation of a first spectral comb confirms the versatility of this molecular complex and highlights its potential for use in advanced spectral tailoring techniques. Four burn pulses were sequentially applied with a frequency separation of 3 MHz, revealing the frequency comb within the inhomogeneous broadening of BB1. Figure 4.48(b) illustrates a fit to the resulting spectral comb, confirming the adjusted frequency separation of the pulse sequence. In conclusion, these findings demonstrate that BB1 possesses high potential as a molecular-based quantum system. However, further investigations are still required and include steps toward a full optical and spin characterization.

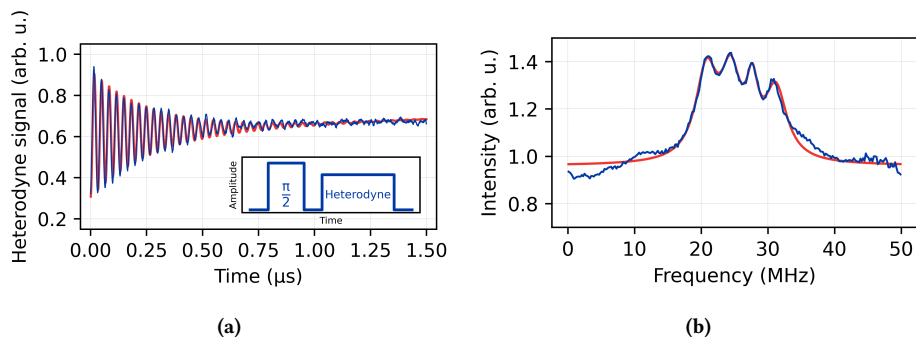


Figure 4.48: FID and frequency comb preparation of BB1. (a) Detected FID signal after resonant excitation with an optical $\pi/2$ pulse, illustrating the rapid dephasing of the ensemble dipoles and enabling the extraction of $T_{2,o,\text{(FID)}}^* = (268 \pm 2)$ ns. The inset represents the applied pulse sequence. (b) Spectral comb observed under sequential burn pulse excitation, showing the formation of multiple spectral holes, which are spaced by a frequency of 3 MHz. Both measurements were performed at a temperature of 4.2 K.

4.3.5. Analysis of the molecular complex $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$

The final molecular system studied in this thesis is the homodinuclear Eu^{3+} complex $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$, which is the structural and synthetic counterpart of BB1. Hereafter, the molecular compound $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$ is referred to as **BB3**. Both molecules were prepared and characterized alongside each other to be included in a joint publication with our collaborators, which is currently under preparation [132].

In BB3, two Eu^{3+} ions are each coordinated by three btfa ligands (4,4,4-trifluoro-1-phenyl-1,3-butanedione) through oxygen atoms, and symmetrically bridged by a bpim ligand (2,2'-bipyrimidine) coordinating via nitrogen atoms. Figure 4.49(a) and (b) illustrate the molecular structure of BB3. Single-crystal X-ray diffraction analysis reveals that each Eu^{3+} ion adopts an eight-coordinate environment with a distorted square antiprismatic geometry. The coordination polyhedron exhibits an approximate D_{4d} point group symmetry. The bpim ligand acts as a tetradentate N_4 -donor, linking the two Eu^{3+} ions symmetrically at a distance of about 6.914 Å, resulting in a well-defined homodinuclear structure. BB3 crystallizes in the triclinic space group $P\bar{1}$, with two dinuclear molecules per unit cell [133]. The asymmetric nature of btfa ligand fields enhances the electric dipole transition probability, while the presence of trifluoromethyl $-\text{CF}_3$ groups contributes to lower non-radiative decay losses by reducing the vibrational degrees of freedom. In addition, extensive hydrogen bonding via C–H, N–H, and O–H groups form two-dimensional structures through intermolecular interactions, suppressing high-energy vibrational modes (in C–H, N–H, and O–H bonds) and thus improving the PL properties of the respective molecule [133]. Further details on the

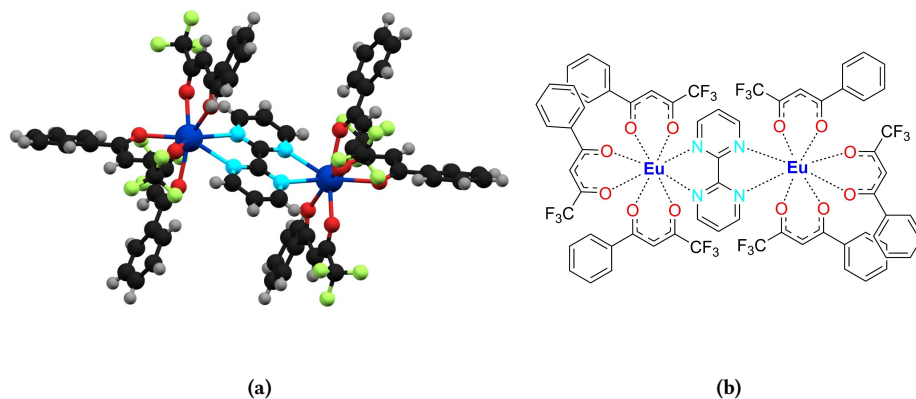


Figure 4.49: Molecular structure of $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$. (a) X-ray crystal structure of a single dinuclear $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$ molecular complex. Europium is shown in blue, oxygen in red, nitrogen in cyan, fluorine in green, carbon in black, and hydrogen in gray. (b) Planar representation of the dinuclear molecular structure. The figure was provided by our collaborator **Dr. Barbora Brachnakova**.

synthesis and crystallographic analysis of this molecular compound are presented in our upcoming publication [132].

The optical characterization of this molecular complex began with the identification of the main PL transitions. The room-temperature emission spectrum is illustrated in Figure 4.50(a). As in the case of BB1, the expected $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions up to $J = 6$ could be observed. However, the primary difference becomes apparent in Figure 4.50(b), where the coherent $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition possesses a higher intensity than the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, thus indicating that the Eu^{3+} centers sit in a symmetrically favorable coordination environment. Although BB3 was analyzed to feature a D_{4d} point group symmetry, which constitutes the same case as for BB1, the observation of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition suggests two potential explanations: according to Binnemans *et al.* [48], most Eu^{3+} -based materials were observed in a C_n , C_{nv} and C_s symmetry sites, meaning that BB3 (and also BB1) could possess a symmetry site of these point groups, which partially allow the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. The second explanation could stem from the fluorinated btfa ligand fields, which locally introduce a strong asymmetry as well as coordination distortion and hence, fulfill the requirements of this transition. The latter could be the reason, why the branching ratio is significantly stronger in the dinuclear complex than in the mononuclear one. The electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is observed at a center wavelength of 579.627 nm, with a linewidth of (0.328 ± 0.003) nm and a branching ratio of 1.30 %. The branching ratio of BB3 represents the largest value observed so far among the investigated Eu^{3+} -based molecular materials.

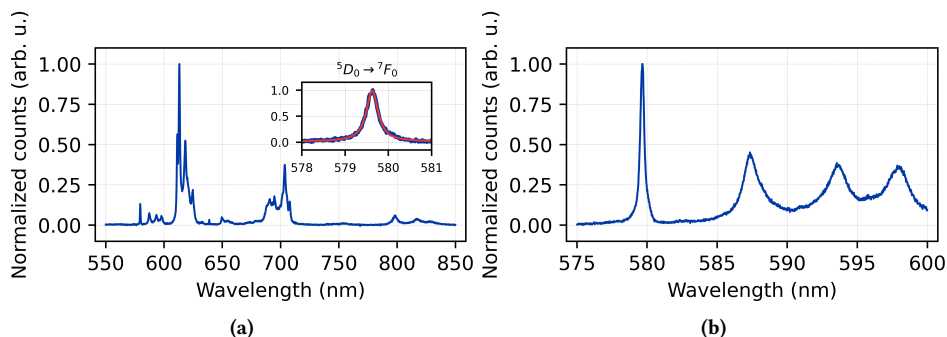


Figure 4.50: Photoluminescence spectra of BB3. (a) Room-temperature emission spectrum showing all resolved $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions up to $J = 6$, featuring a higher intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ compared to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. The inset represents a fit to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition centered around 579.627 nm. (b) Zoomed-in view of the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition region, showing that the branching ratio for the coherent $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is relatively larger compared to previous molecular compounds. Both spectra are normalized to their respective maximum intensities.

The ensemble spectroscopy of BB3 was performed directly after our measurements on BB1. The sample was measured again in the Sionludi cryostat at temperatures of about 100 mK. BB3 also forms a microcrystalline powder, which is introduced into our modified sample holder based on the phosphor bronze casing design to provide better thermal contact. Figure 4.51(a) shows the PLE scan, resulting in a peak at 579.944 nm, corresponding to 516 933.52 GHz, and an inhomogeneous linewidth of (13.41 ± 0.05) GHz. For different samples, the inhomogeneous line was also observed within a frequency range of approximately 516 922 GHz to 516 933 GHz. The inhomogeneous linewidth of

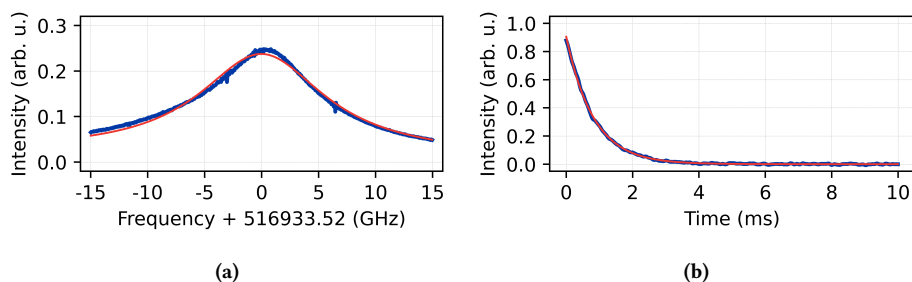


Figure 4.51: Inhomogeneous linewidth and excited-state lifetime of BB3. (a) Inhomogeneous line scan of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition at 100 mK, revealing a Lorentzian line shape (red) centered around $\lambda = 579.944$ nm with a linewidth of (13.41 ± 0.05) GHz. (b) Optical excited-state lifetime $T_{1,0}$ extracted from the decay of the fluorescence signal at the end of the burn pulse in SHB measurements, yielding a value of (819 ± 1) μs . Both measurements were performed at a temperature of 100 mK.

4. Ensemble spectroscopy of Eu^{3+} -based molecular complexes

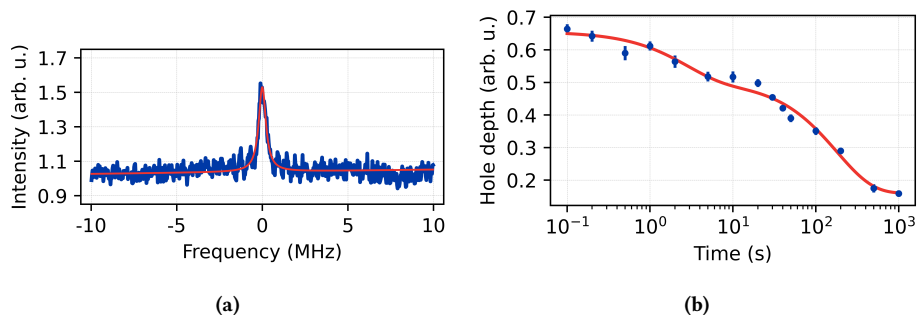


Figure 4.52: SHB and hyperfine lifetime of BB3. (a) An SHB measurement was performed using a 500 ms burn and 200 ms probe pulse. The resulting spectral hole was fitted with a Lorentzian function, yielding a narrow hole width of (0.50 ± 0.02) MHz and a maximum hole contrast of approximately 50 %. (b) The time evaluation of the hole depth as a function of the delay time between burn and probe pulses reveals a double-exponential relaxation with two time components of the hyperfine lifetime: $T_{1,s(\text{short})} = (2.66 \pm 1.19)$ s and $T_{1,s(\text{long})} = (181.26 \pm 28.75)$ s. Both measurements were performed at a temperature of 100 mK.

BB3 is comparable to the linewidth of BB1 as well as that of the other samples, meaning that the structural disorder is approximately at the same level and may be improved when growing macroscopic crystals. As for BB1, the inhomogeneous line could also be probed in transmission and yielded similar linewidths. Additional studies of the inhomogeneous linewidth were not performed. The excited-state lifetime was extracted from our SHB measurements. Figure 4.51(b) illustrates the decay at the end of the burn pulse, which was fitted with a monoexponential function, yielding an optical lifetime of approximately $T_{1,o} = (819 \pm 1)$ μs . The lifetime estimated in the work of Ilmi *et al.* [133] is about 762 μs . Slight variations in the optical lifetime can be attributed to the preparation methods of the sample.

The homogeneous linewidth was accessed via SHB measurements using our standard pulse sequence composed of a 500 ms burn and a subsequent 200 ms probe pulse, followed by an erasing sequence. The narrowest spectral hole obtained for BB3 was recorded with a laser power of 2.5 μW and is shown in Figure 4.52(a), featuring a hole width of (500 ± 20) kHz, which is close to the frequency-stabilized laser linewidth of ~ 100 kHz. This corresponds to a homogeneous linewidth of (250 ± 10) kHz and thus a $T_{2,o}^* = (1.27 \pm 0.05)$ μs . The final measurement in this cooldown was the extraction of the hyperfine lifetime. The decay of the spectral hole depth was recorded as a function of the time delay between the burn and probe pulses. Figure 4.52(b) represents the fitted time evolution of the hole depth, yielding two hyperfine lifetime components: a short time constant of $T_{1,s(\text{short})} = (2.66 \pm 1.19)$ s and a long time constant of $T_{1,s(\text{long})} = (181.26 \pm 28.75)$ s.

In a second cooldown within the Sionludi cryostat at temperatures of about 100 mK, a new sample was prepared following the previous procedure to perform further optical coherence measurements, including an FID measurement and a two-pulse photon echo.

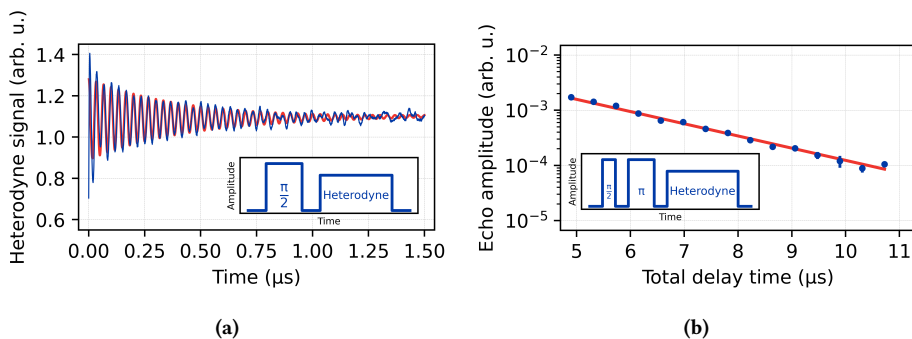


Figure 4.53: FID and photon echo of BB3. (a) Detected FID signal after resonant excitation with an optical $\pi/2$ pulse, illustrating the rapid dephasing of the ensemble dipoles and enabling the extraction of $T_{2,o,\text{(FID)}}^* = (421 \pm 9)$ ns. The inset represents the applied pulse sequence. (b) The echo amplitude is displayed as a function of total delay time τ , from which the optical coherence time $T_{2,o}$ of (1.96 ± 0.07) μs is extracted from a linear fit (logarithmic y-axis). The inset shows the schematic of the two-pulse photon echo sequence, consisting of a $\pi/2$ excitation pulse, a π rephasing pulse, and a final readout pulse, which captures the echo as a beating signal via a heterodyne detection technique. Both measurements were performed at a temperature of 100 mK.

Figure 4.53(a) illustrates the decaying FID beating signal after applying a $5 \mu\text{s}$ $\pi/2$ excitation pulse and a $2 \mu\text{s}$ readout pulse at an optical power of 70 mW. The obtained dephasing time $T_{2,o,\text{(FID)}}^*$ is about (421 ± 9) ns. In addition, we successfully measured a photon echo with this molecule, a result that had previously only been achieved with SKR520. A similar pulse sequence was applied: a 800 ns $\pi/2$ pulse followed by a 900 ns π rephasing pulse and a readout pulse, with the echo signal acquired using heterodyne detection. The decay of the echo amplitude as a function of time was fitted with a linear function on a logarithmic y-scale, resulting in an optical coherence time $T_{2,o}$ of (1.96 ± 0.07) μs , as shown in Figure 4.53(b). This result is on the same order of magnitude as the photon-echo-based optical coherence time measured for SKR520, with room for improvement upon optimizing several pulse parameters.

In conclusion, these results highlight the promising optical properties of the molecular complex BB3. Moreover, due to the presence of two Eu^{3+} centers, it holds the potential for implementing a two-qubit gate based on electric dipole–dipole interactions [33, 134].

Table 4.2: Comparison of key spectroscopic properties of the investigated Eu^{3+} -based molecular complexes throughout this thesis. For each molecule, only the best-obtained values of the respective property are listed. The star in the last column for the optical coherence $T_{2,o}$ denotes that the value was extracted either from SHB or FID measurements. The abbreviations PGS and BR stand for point group symmetry and branching ratio, respectively.

Molecule	PGS	BR (%)	Γ_{inh} (GHz)	Γ_h (MHz)	$T_{1,o}$ (μs)	$T_{1,s}$ (s)	$T_{2,o}$ (μs)
SKR520	C_{2v}	0.16	1.95	0.125	520	4.41/122	2-3
SKR127	C_{3v}	> 0.16	90	2.8	320	7/460	*0.114
SKR147	C_{2v}	0.11	16.44	1.55	1425	0.31/41.39	*0.205
BB1	D_{4d}	0.14	11.97	0.595	747	4.25	*0.535
BB3	D_{4d}	1.30	13.41	0.25	819	2.66/181.26	1.96

4.4. Conclusion of the investigated molecular complexes

The following section primarily presents a comparative overview of the optical and spin properties of Eu^{3+} -based molecular systems investigated in this thesis. Table 4.2 summarizes all currently measured optical characteristics of the molecular compounds discussed in the preceding sections. While several promising properties are observed, they are not yet combined within a single molecule.

Figure 4.54 depicts the branching ratio as a function of the optical coherence time $T_{2,o}$, and includes not only all Eu^{3+} -based molecular materials investigated within this thesis, but also additional reference systems. These comprise $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ nanoparticles [34, 135] and molecular complexes, both of which are currently being studied by colleagues within our research group. Among them is the $[\text{Eu}(\text{dbm})_3(\text{bipy})]$ complex, referred to as **7-Eu**, in which the Eu^{3+} ion is coordinated by three dibenzoylmethane (dbm) ligands and one auxiliary 2,2'-bipyridine (bipy) ligand [136]. This compound was provided through a collaboration with **Professor Michael Seitz** (University of Tübingen). The top-right corner of the plot represents the optimal regime for material systems. Unfortunately, none of the Eu^{3+} -based materials currently fulfills both criteria simultaneously.

However, beyond the optical performance, several of these systems exhibit encouraging characteristics in terms of nuclear spin lifetimes. If the hyperfine structure of each system can be precisely determined, spin characterization could be carried out systematically, potentially revealing desired nuclear spin coherence times $T_{2,s}$. Coherent nuclear spin control has finally been demonstrated in SKR520, opening up not only new opportunities for further analysis, for instance, probing the spin bath environment, but also for applying these practically validated spectroscopic techniques to other molecules.

The current nuclear spin coherence time $T_{2,s}$ of 2 ms is highly encouraging and could be further extended through optimization and advanced pulse sequences. Compared to other spin-bearing molecular systems [35], SKR520 exhibits the longest spin coherence time so far. However, this does not automatically make it the most promising system, since its optical properties, including the branching ratio, can still be considered rather

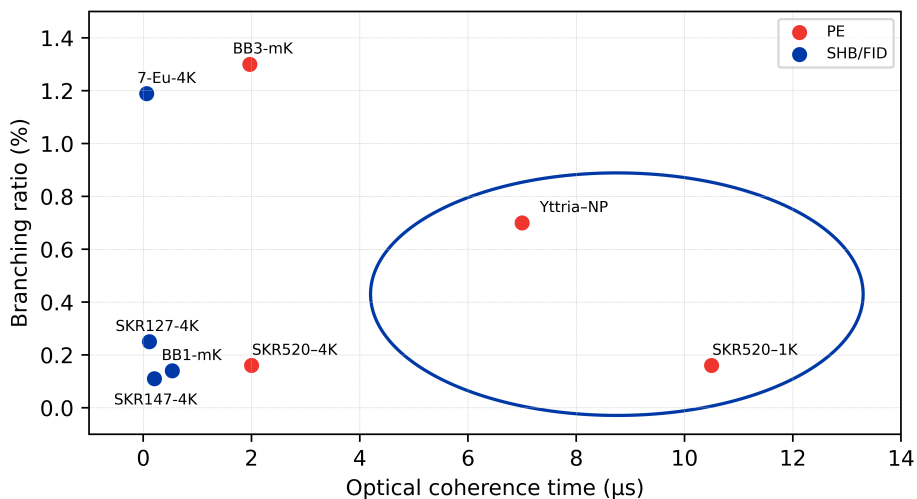


Figure 4.54: Comparison of Eu^{3+} -based materials. The plot illustrates the branching ratio as a function of the optical coherence time $T_{2,o}$ for several Eu^{3+} -based materials investigated within our research group, including the reported coherence time of SKR520. The color of the dots denotes the measurement technique used to determine the optical coherence time $T_{2,o}$: red represents photon echo (PE) and blue SHB or FID measurements. The corresponding sample and temperature values are positioned either above or below the dot. The favorable region is the upper right part of the graph. Unfortunately, not many materials are found there. The emerging field of REI-based molecular systems requires more data in terms of optical and spin characterization to populate this graph and thus find more promising candidates to be integrated into future quantum information applications.

limited. Here, the field of chemical engineering offers a clear path for improvement. Also noteworthy is the dinuclear complex BB3, which shows some of the best optical properties after SKR520. Due to the presence of two Eu^{3+} centers, it could potentially serve as a two-qubit gate system controlled by electric dipole–dipole interactions.

Nevertheless, all molecules still require further investigation to confirm the reproducibility of their intrinsic properties. With our improved and refined spectroscopy techniques, it is likely that the currently observed characteristics can be improved even further before making a final assessment of their suitability for practical quantum technologies. Although the initial analysis did not reveal an ideal candidate for an optically addressable, spin-bearing molecular system, the results form a solid groundwork for the ongoing development of molecular materials. Future studies should aim to complete the optical characterization and extend the investigation toward systematic analysis of spin coherence properties in order to determine potentially suitable molecular quantum systems.

4. Ensemble spectroscopy of Eu^{3+} -based molecular complexes

At this stage, we consider this research direction extremely promising. Once the fundamental spectroscopic methods are fully established, the investigation of new molecular systems can proceed in an accelerated manner. This will enable the targeted design and synthesis of tailored molecules, allowing suitable systems to be identified much more efficiently for integration into future quantum technologies.

5. Implementation of a new microcavity design for spectroscopy

During the investigation of individual molecular emitter systems, considerations were also made regarding how these samples could be integrated into an optical resonator. To realize future concepts in applicable quantum technologies, as proposed in the SQUARE project, optical cavities play a crucial role. They enhance light-matter interaction, which is particularly required in the case of Eu^{3+} ions due to its weak branching ratio and long excited-state lifetime. This enhancement can be harnessed for different spectroscopic schemes, including the creation of an efficient spin-photon interface, where the emitter system acts as a stationary node. Coherent emission of indistinguishable photons from such a cavity can then be used to link multiple cavities via optical fibers [78], which constitutes an essential step toward achieving quantum networks.

Among the various promising concepts in realizing such architectures, fiber-based Fabry-Pérot microcavities offer significant advantages [89]: wide tunability of cavity parameters, open-access design for versatile sample integration, and high compatibility with optical and cryogenic systems. This chapter presents a novel cryo-compatible design for a fiber-based Fabry-Pérot microcavity. The conceptual groundwork was laid during my Master's thesis.

Integrating fiber-based cavities with cryogenic environments presents unique challenges. These include maintaining precise positioning on the sample despite thermal contraction during a cooldown, and ensuring high cavity stability to allow for spectroscopy without any disturbances. Typically, our cavities, which employ a plano-concave design, incorporate multiple piezo stacks in order to provide scanning capabilities. The new design addresses the mentioned issues by minimizing the number of moving components and consolidating the degrees of freedom into a single, scannable piezo tube, which is a common approach in scanning tunneling microscopy. In addition, a massive base block provides high passive mechanical stability, which can optionally be improved through active stabilization feedback loops.

The initial implementation and testing of the setup were carried out by **Fabian Heizmann** during his Bachelor's thesis. Afterwards, the system was stepwise improved by performing first characterization measurements at both room temperature and at cryogenic temperatures down to the millikelvin regime. During the course of my doctoral work, two Master's students, **Weizhe Li** and **Xiaoyu Yang**, successfully integrated

first molecular Eu^{3+} -based samples into our room-temperature cavity setups using two different approaches, which resulted in encouraging spectroscopic measurements.

This chapter begins with a brief overview of the relevant optical resonator theory, followed by a detailed description of the cavity setup and the respective control system. Afterwards, initial characterization results of the cavity performance are presented. The chapter concludes with an outlook on cavity spectroscopy of Eu^{3+} -based molecular complexes, highlighting the progress achieved so far and the potential for future developments in this direction.

5.1. Brief theoretical summary on optical resonators

In this section, only the basic principles required for understanding the principles of a fiber-based microcavity are outlined. For a more in-depth theoretical treatment, the reader is referred to the work of my colleagues, in particular, **Maximilian Pallmann** [137] and **Timon Eichhorn** [34], or to specialized literature such as the book by **Saleh** and **Teich** [138].

Parameters of an optical resonator: Our cavities are based on the Fabry–Pérot interferometer, which is generally formed by two parallel, highly reflective mirrors separated by a distance d . When the optical path inside the resonator matches integer multiples of half the wavelength, the formation of standing waves is supported, and thus resonances can be observed. This resonance condition incorporates the *free spectral range*:

$$\Delta\nu = \frac{c}{2d}, \quad (5.1.1)$$

which is the spacing between two consecutive resonance frequencies. Real cavities exhibit losses $\mathcal{L}_{\text{tot}}$ from mirror transmissions T_1 and T_2 , scattering, and absorption at the mirror surfaces, leading to a broadening of the resonance linewidth $\delta\nu \propto \mathcal{L}_{\text{tot}}/d$. One essential figure of merit, which quantifies the performance of a cavity, is given by the *finesse*:

$$\mathcal{F} = \frac{\Delta\nu}{\delta\nu} = \frac{2\pi}{\mathcal{L}_{\text{tot}}}. \quad (5.1.2)$$

The finesse reflects the number of round trips that light travels inside the cavity before outcoupling through the mirrors. This is the reason why it can be related to the photon lifetime within a cavity $\tau_{\text{rd}} = d\mathcal{F}/\pi c$ and the corresponding decay rate as the inverse of the lifetime $\kappa = 1/\tau_{\text{rd}} = 2\pi\delta\nu$. Besides the finesse, the *quality factor* Q is commonly used to characterize the cavity performance. It expresses the ratio of energy stored in the cavity to the energy lost per round trip and is defined as:

$$Q = \frac{\nu}{\delta\nu} = q \cdot \mathcal{F}, \quad (5.1.3)$$

where $q = d/(\lambda/2)$ is the longitudinal mode order of a resonance frequency ν_q . According to Equation 5.1.3, the quality factor scales linearly with the mode order and thus with the cavity length.

In practical implementations, optical resonators made of two planar mirrors are unstable due to strict alignment requirements. Replacing one or both mirrors with concave mirrors that possess a Radius of curvature (ROC) improves the stability, since even slightly angled beams allow for self-reproducing modes and remain confined within the cavity upon reflection. The *stability condition* for a cavity with mirror radii of curvature ROC_1 and ROC_2 separated by a distance d is described by the following expression:

$$0 \leq \left(1 - \frac{d}{\text{ROC}_1}\right) \left(1 - \frac{d}{\text{ROC}_2}\right) \leq 1. \quad (5.1.4)$$

In our specific case of a fiber-based cavity, where one mirror is a macroscopic planar mirror and the opposing mirror is a fiber with a concave profile at the end facet shaped via CO₂ laser machining, the stability condition simplifies to:

$$0 \leq \left(1 - \frac{d}{\text{ROC}}\right) \leq 1, \quad (5.1.5)$$

with ROC as the radius of curvature of the concave fiber mirror and d as the cavity length. This implies that the cavity remains stable as long as the mirror separation does not exceed the ROC of the fiber mirror.

Gaussian beams: When curved mirrors are used, the resonator modes can no longer be accurately described by plane waves, as in the case of two planar mirrors. Instead, the spatial confinement and curved wavefronts can be described by Gaussian beams, which are solutions to the paraxial Helmholtz equation. As implied by the name, the lateral intensity distribution is determined by a Gaussian function. The key parameters include:

- **Beam waist:** w_0 is the smallest beam radius at the focus point.
- **Rayleigh length:** $z_0 = \pi \cdot w_0^2 / \lambda$ is the distance over which the beam remains nearly collimated, meaning the region can be treated as plane waves.
- **Beam radius:** $w(z)$ describes the radius at the position z from the beam waist (spatial spread).
- **Wavefront curvature:** $R(z)$ defines the curved wavefront of the Gaussian beam. For $z \rightarrow 0$, R approaches ∞ , resulting in a planar wavefront.
- **Gouy phase:** $\theta(z)$ constitutes an additional phase shift acquired during propagation within the cavity. As a consequence, the points of equal phase are on the curved wavefronts.

Considering now the resonance condition for a plano-concave cavity supporting Gaussian modes, the Gouy phase must be taken into account in addition to the optical path length. This leads to the following modified expression for the resonance frequencies of the cavity:

$$\nu_q = \Delta\nu \left(q + \frac{\Delta\theta}{\pi} \right), \quad (5.1.6)$$

with $\Delta\theta = [\theta(z = d) - \theta(z = 0)]$.

Hermite-Gaussian modes: In addition to the fundamental Gaussian modes, optical cavities can support higher-order transverse modes, known as Hermite-Gaussian modes. These are solutions to the paraxial Helmholtz equation and are characterized by the product of Hermite polynomials with the Gaussian envelope, leading to spatially structured intensity distributions. The resonance frequencies of these higher-order Hermite-Gaussian modes are described by:

$$\nu_{(q,m,n)} = \Delta\nu \left(q + (m + n + 1) \frac{\Delta\theta}{\pi} \right), \quad (5.1.7)$$

where q is the longitudinal mode number, and m and n are the transverse mode indices. In ideal spherical cavities, modes with the same $m + n$ are degenerate. In contrast, real cavities exhibit slightly different boundary conditions, as the fiber mirrors often possess a small ellipticity in their concave profile, typically introduced during laser machining. This asymmetry results in a lift of the degeneracy, thus making modes (m, n) and (n, m) distinguishable [137].

Fundamentals of light-matter interaction: Our overall aim is to integrate molecular structures into fiber-based Fabry–Pérot microcavities in order to explore their optical properties under cavity-mediated conditions. To understand these processes, it is essential to first gain insight into the fundamental principles underlying light-matter interaction in optical cavities.

So far, we have only considered empty cavities, where no emitter or refractive medium is present. Introducing a quantum emitter into the resonator opens up a new theoretical chapter of Cavity quantum electrodynamics (cQED), where the interaction is governed by the cavity-emitter coupling strength expressed as follows:

$$g_0 = \sqrt{\frac{\pi\mu_{12}^2\nu}{\epsilon_0\hbar V_m}}, \quad (5.1.8)$$

with ν as the resonance frequency of the cavity mode, μ_{12} as the transition dipole moment from the electronic ground state $|g\rangle$ to the excited state $|e\rangle$, and $V_m = \pi w_0^2 d/4$ as the mode volume of the cavity. A more detailed description can be found in the book by **Mark Fox** [139], but also the theses of **Maximilian Pallmann** [137] and **Timon**

Eichhorn [34] provide more insights. Here, we only want to emphasize which effects are present in a coupled cavity-emitter system. In addition to the coupling strength g_0 , the cavity decay rate κ and the total emitter dephasing rate $\propto \gamma + \gamma^*$, which is composed of the spontaneous emission rate and the pure dephasing rate, respectively, are introduced in order to describe different regimes of interaction. When only a specific optical transition is considered, e.g., the $^5D_0 \rightarrow ^7F_0$ transition in Eu^{3+} , the effective coupling strength is modified to $g = \sqrt{\zeta} g_0$, where ζ denotes the branching ratio. The interaction regimes can thus be categorized as follows:

- **Strong coupling:** $2g \gg \gamma + \gamma^* + \kappa$

In this regime, the coupling strength is much stronger than the occurring dephasing mechanisms, so that photons can be trapped long enough for coherent energy exchange between cavity and emitter (re-absorption of photons). This process enables phenomena such as vacuum Rabi oscillations.

- **Weak coupling:** $2g \ll \gamma + \gamma^* + \kappa$

In this case, dissipation limits the interaction, and the behavior of the system is determined particularly by the emitter and cavity linewidths:

- **Bad cavity regime:** $\delta\nu_{\text{em}} \ll \delta\nu_{\text{c}}$

Photon losses from the cavity dominate in this regime.

- **Bad emitter regime:** $\delta\nu_{\text{em}} \gg \delta\nu_{\text{c}}$

Emitter dephasing is the main limitation, as the emitter linewidth is much broader. This is typically the case when we investigate our emitter systems within the cavities at room temperature.

- **Comparable linewidths:** $\delta\nu_{\text{em}} \approx \delta\nu_{\text{c}}$

Both the emitter and cavity linewidths are broad and must be considered when calculating loss contributions or enhancement factors.

In the following, we will focus exclusively on the weak coupling regime, and specifically on the principle of the so-called *Purcell effect*, which describes the enhancement of the spontaneous emission due to the modified photonic density of states inside the resonator.

Spontaneous emission and Purcell effect: The spontaneous emission rate of a quantum emitter can be derived by applying time-dependent perturbation theory, which treats the interaction between the dipole moment of the emitter $\mathbf{d} = -e\mathbf{r}$ and the quantized vacuum electric field $\mathbf{E}_{\text{vac}}$ as a weak perturbation. The transition probability is given by *Fermi's golden rule* [137]:

$$\gamma_0 = \frac{2\pi}{\hbar} M_{12}^2 \rho(\omega), \quad (5.1.9)$$

where $M_{12} = \langle \mathbf{d} \cdot \mathbf{E}_{\text{vac}} \rangle$ denotes the transition matrix element, and $\rho(\omega)$ is the photonic density of states at the transition frequency of the emitter. In free space, this leads to a spontaneous emission rate, which can be summarized as:

$$\gamma_0 \equiv \frac{1}{\tau_r} = \frac{\mu_{12}^2 \omega^3}{3\pi\epsilon_0 \hbar c^3}, \quad (5.1.10)$$

with τ_r as the radiative lifetime of the emitter, μ_{12} as the transition dipole moment, and the factor $1/3$ arising due to the average over all possible dipole orientations in free space.

When an emitter is placed inside a resonant optical cavity, the density of states is affected due to emitter-cavity coupling, which leads to a change in the spontaneous emission rate known as the *Purcell effect*:

$$\gamma_c = \frac{2\pi}{\hbar^2} \int_0^\infty M_{12}^2(\omega) \rho(\omega) \Lambda(\omega) d\omega. \quad (5.1.11)$$

Here, $\Lambda(\omega)$ describes the density of states of the emitter. The emission rate in the cavity becomes:

$$\gamma_c = C \cdot \gamma_0, \quad (5.1.12)$$

where C is the *Purcell factor* and is typically given by the following expression [137]:

$$C_0 = \xi^2 \frac{3}{4\pi^2} \left(\frac{\lambda}{n} \right)^3 \frac{Q}{V_m} = \xi^2 \frac{6}{\pi^3} \left(\frac{\lambda}{n} \right)^2 \frac{\mathcal{F}}{w_0^2}, \quad (5.1.13)$$

with ξ as the dipole orientation factor between the emitter and the polarization of the cavity field, λ as the transition wavelength, and n as the refractive index of the corresponding medium of the emitter. For $\xi = 1$, this expression corresponds to the *ideal Purcell factor* C_0 , assuming exact frequency matching between the emitter transition and the cavity resonance as well as optimal dipole alignment with the electric field of the cavity. An alternative description of the Purcell factor involves all the coupling mechanisms and decay rates of the system:

$$C_0 = \frac{4g_0^2}{\kappa\gamma_0}. \quad (5.1.14)$$

These expressions highlight that the spontaneous emission can be significantly enhanced in the weak coupling regime by engineering cavities with high quality factors Q and small mode volumes V_m or similarly with high-finesse cavities, which confine light to spot sizes with very small beam waists w_0 .

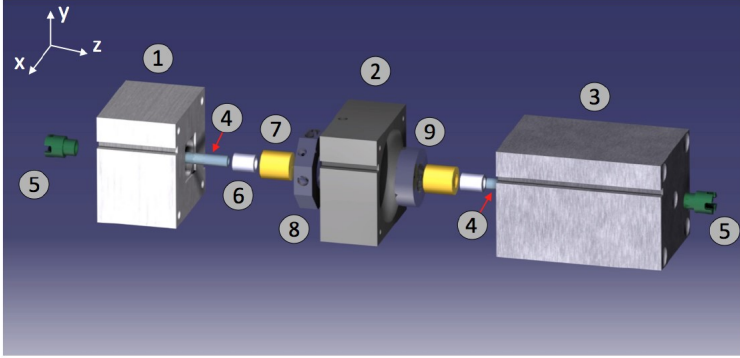
This concludes the theoretical framework on optical cavities coupled to emitter systems, and further details such as the specific cases of bad cavity or bad emitter regimes are not discussed here and can be found in the previously mentioned and referenced literature.

5.2. Design of a novel robust fiber-based Fabry–Pérot microcavity

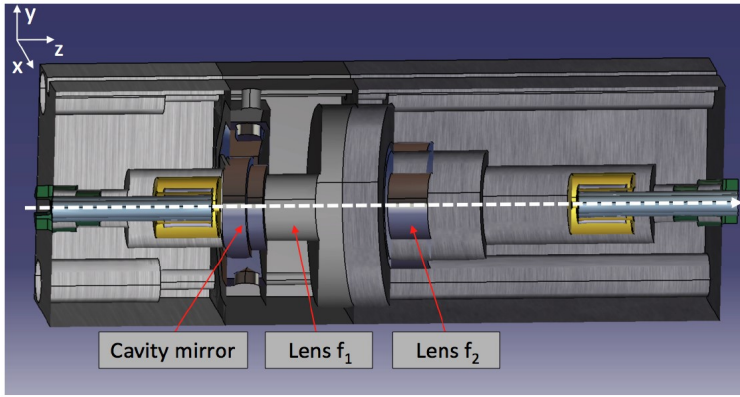
The newly developed fiber-based Fabry–Pérot microcavity was originally designed for operation in our exchange gas dipstick cryostat, which directly influenced the final geometry of the cavity. In its original form, the overall dimensions were 30 mm × 30 mm × 96.5 mm to fit into the tube of the dipstick with a diameter of about 49 mm. To ensure thermal compatibility and mechanical stability under cryogenic conditions, titanium is used as the base material for all components due to its low thermal expansion coefficient ($\approx 8.2 \cdot 10^{-6} \text{ K}^{-1}$) and robustness.

The setup initially consisted of three main blocks: an input block (1) incorporating the laser-machined fiber, a central block (2) housing an octagon-shaped mount for a macroscopic planar mirror, and an output block (3) for collecting the transmitted light. The central difference compared to our conventional cavities is the implementation of piezo scanner tubes (4) in order to preserve lateral 2D raster scanning combined with a scan in Z direction for cavity length control. While in other cavity setups the scanning capabilities are realized via many piezo stacks, the piezo tube design allows us to reduce the number of components and thus many tunable degrees of freedom to increase the passive stability. In general, these piezo tubes provide precise spatial control and are fabricated from materials ($\sim 2 \cdot 10^{-6} \text{ K}^{-1}$) compatible with titanium and in turn for cryogenic operation. Figure 5.1(a) shows the initial concept of the cavity represented in the exploded view.

Coarse cavity length adjustments are achieved through both the wreath-like piezo tube holders (5) and the threaded fiber mounts (6)–(7), where the threaded mount (6) is glued to the front of the piezo scanner tube and the cap (7) houses the needle containing the cavity fiber. Meanwhile, the macroscopic planar cavity mirror is integrated into the spring-loaded octagon-shaped holder (8), which can be accurately adjusted to the desired lateral mirror position via two fine-threaded screws. The transmitted light is collected and focused onto a multimode fiber by a two-lens system consisting of a collimation lens f_1 mounted in the middle block and a focusing lens f_2 screwed into the adjustable mount (9), thereby increasing the outcoupling efficiency. Figure 5.1(b) illustrates the cross-sectional view of the cavity design as well as the excitation and collection paths. All mechanical components are custom-fabricated by the mechanical workshop of the *Physics Institute* via computer numerical control machining. The modular design supports the integration of membrane-like or thin-film structures to ensure that the cavity fiber remains positioned above the sample when thermal drifts occur. Before a cooldown, the cavity must be coarsely aligned for cavity spectroscopy while taking thermal drifts into account. If suitable sample regions are identified, then the individual blocks must be tightly fixed via the corresponding screws to maintain a high passive stability during cryogenic operation.



(a)



(b)

Figure 5.1: Exploded and cross-sectional views of the cryo-compatible cavity design. (a) Exploded view of the cryo-compatible fiber-based cavity design, showing the modular structure. The setup consists of three main blocks: input (1), middle (2), and output block (3). Two piezo scanner tubes (4) are mounted via wreath-like holders (5). The threaded mount (6) is glued to the front of the piezo scanner tube. The cap (7) is screwed onto this mount and holds the needle, into which the cavity fiber is glued. The cavity mirror is housed in an octagon-shaped mirror holder (8). (b) Cross-sectional view of the fully assembled system, illustrating the optical path (white dashed line) through the cavity mirrors and the integrated lens setup. A collimation lens f_1 , which is mounted in the middle block, and a focusing lens f_2 , which is screwed into the adjustable lens mount (9), ensure optimal coupling efficiency into the multimode fiber. Both figures are taken from [140].

However, following the first experimental trials, the concept of the third output block was omitted. It proved challenging to synchronize excitation and collection with this setup, particularly during 2D raster scanning, due to the arising complexity in fiber alignment. As a result, the subsequent design focused on simplifying the geometry and optimizing light collection via the integration of a cryo-compatible detector or via the free-space output windows when installing the cavity into the table-top dilution refrigerator.

5.3. Integration into optical system and cavity performance

In this section, we briefly recapitulate the procedures involved in the first implementation of the cavity setup, originally carried out by **Fabian Heizmann** during his Bachelor's thesis. This includes the preparation steps such as gluing the piezo scanner tube into the wreath-like component and integrating the fiber mirror, followed by the assembly of the system into the optical setup. Finally, we present initial characterization measurements conducted at both room temperature and under cryogenic conditions.

5.3.1. Preparation of the piezo scanner tube

The piezo scanner tube³⁷ has a length of 30 mm and an outer diameter of 3.2 mm. In order to perform lateral scanning, the tube features four segmented outer electrodes, which can be driven with voltages up to ± 250 V, enabling a maximum lateral (XY directions) displacement of ± 35 μm and an axial expansion (Z direction) of up to 9 μm . From this, a linear approximation yields a normalized displacement of about 70 nm V^{-1} in lateral and 18 nm V^{-1} in axial directions. These characteristics allow for a 2D scanning window of about 1000 μm^2 , while being simultaneously capable of scanning over a few longitudinal mode orders of the cavity. The high voltages are supplied by an amplifier³⁸ specifically designed for such piezo scanner tubes.

The electrical connection of the piezo electrodes was carried out by the electronics workshop of the *Physics Institute*. The major challenge during this process is not to overheat the piezo ceramic material, which could lead to malfunctions, and to create very small soldering points so that the tube can fit into the wreath-like part for gluing.

The gluing process involves a two-step procedure: the first step is the electrical insulation of the piezo tube from the metallic parts using a two-component epoxy³⁹, followed by oven curing at 65°C for 2 h. After verifying the electrical insulation, the piezo is

³⁷ Model: PT230.94, purchased from *PI Ceramic*.

³⁸ Model: E-413.61, purchased from *PI Ceramic*.

³⁹ Model: Epo-Tek 301, purchased from *Epoxy Technology*.

inserted into the wreath-like mount and the threaded cylindrical part onto which the counterpart together with the fiber can be screwed and then mechanically fixed in the specifically designed holder for the gluing procedure. This process is crucial, since the gluing of the piezo tube defines the final lateral (angular) alignment of the fiber and is important for stable cavity operation. Although the holder is designed to maintain a good alignment, it still can introduce some deviations. However, when an optimal position is adjusted, the gluing procedure is performed using a second two-component epoxy⁴⁰, which fills the gaps between the respective components by capillary forces. This is followed by oven curing at 65 °C for 3 h [141].

5.3.2. Optical system and control unit

The schematic of the optical setup is shown in Figure 5.2. The laser light is coupled into the cavity via the laser-machined fiber, which is incorporated within a needle-based mount that can be screwed onto the top of the piezo tube. In combination with the opposing macroscopic mirror, the central part of this setup is formed. In order to achieve large Purcell factors, our cavities are specifically designed to reach high finesse through the use of distributed Bragg reflector (DBR) coatings on both the macroscopic mirror and the concave-shaped fiber end facet. A DBR consists of alternating dielectric layers with high and low refractive indices. Each applied coating is only designed for a specific target wavelength. Otherwise, the condition for constructive interference within the individual layers will not be ensured. However, for the correct wavelength, the DBR coatings provide a high reflectance R , resulting in sharp cavity lines and high finesse values. The DBR coatings used within our setup were designed for a center wavelength of 580 nm. When the piezo tube is electrically driven and the resonance condition is fulfilled, then the cavity light can be outcoupled and guided in free space toward a detector. During the experiments, two detectors were used: a conventional APD⁴¹ for room temperature and cryogenic measurements when using the Sionludi cryostat, and a silicon photomultiplier (SiPM) chip⁴². The latter was used during our cryogenic measurements within the exchange gas dipstick, as there is no free-space output window. The chip was installed on top of the cavity setup, and the respective electronics were kept outside to prevent effects occurring in semiconductor electronics at low temperatures. It should be noted that the detector is not directly cryo-compatible and was tested without guarantee for successful operation. Alternatively, the light could also be coupled to a spectrometer⁴³. For the characterization measurements, three diode laser systems with center wavelengths at 532 nm, 580 nm, and 640 nm were available. Due to the design wavelength of the used DBR coatings at 580 nm, the finesse decreases for other laser wavelengths.

⁴⁰ Model: *Epo-Tek 302-3M*, purchased from *Epoxy Technology*.

⁴¹ Model: *APD430A2*, purchased from *Thorlabs*.

⁴² Model: *KETEK PE3315-WBTIA-SP*, purchased from *KETEK*.

⁴³ Model: *Andor Shamrock-500i-D2-SIL-R*, purchased from *Oxford Instruments*.

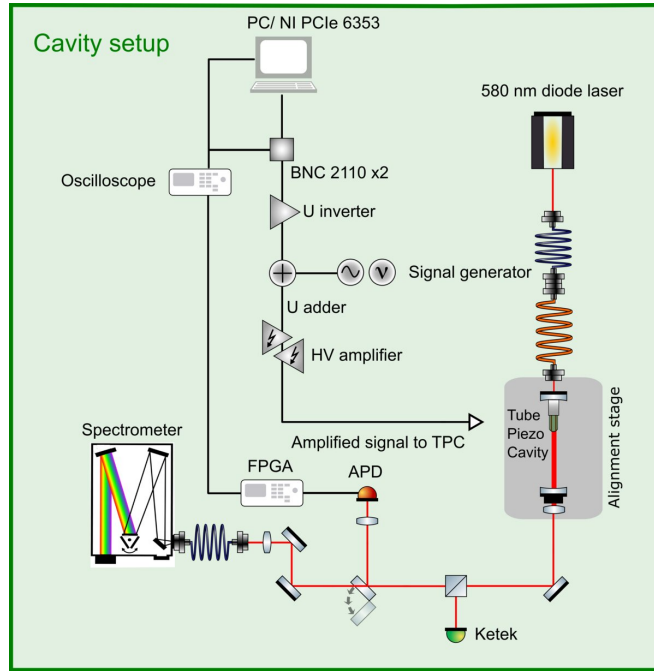


Figure 5.2: Schematic overview of the optical and control setup of the tube piezo cavity. Illustrated schematic of the fiber-based tube piezo cavity (TPC) setup, showing the integration of the central optical and hardware components. The DBR coating of the fibers is designed for a center wavelength of 580 nm. However, for different measurement methods, other laser sources can be fiber-coupled to the cavity. The fiber is mounted in a needle-based holder attached to the piezo tube, which enables 2D raster scanning in XY directions and cavity length modulation in the Z direction. Light coupled out of the cavity can be directed to photodetectors (APD or SiPM) or a commercial spectrometer. The tube piezo is controlled through a Peripheral Component Interconnect Express (PCIe) card. The scan signal is output toward the voltage inverter, which generates four separate signals, one for each electrode of the tube piezo, by providing both the original and the inverted voltages (U inverter) required for the XY movement. For longitudinal Z modulation, a signal from a function generator is added to scan signals using a voltage adder circuit (U adder). The composite signals are then amplified (HV amplifier) before being applied to the piezo tube, enabling simultaneous 2D raster scanning and modulation of the cavity length. The schematic layout was created with Inkscape and the Component Library [93].

The key advantage of the experimental control setup is the ability to monitor the cavity parameters in real time. The GUI is based on the Python script *Fluxi* from **Thomas Hümmer**. The control system requires a PCIe card ⁴⁴, an FPGA ⁴⁵ and two Bayonet

⁴⁴ Model: NI PCIe 6353, purchased from National Instruments.

⁴⁵ Model: StemLab 125-14, purchased from Red Pitaya.

5. Implementation of a new microcavity design for spectroscopy

Neill–Concelman (BNC) connector boxes ⁴⁶ to interface with the analog channels of the employed devices including detectors, oscilloscopes, and piezo amplifiers. Two main applications are supported:

- **Finesse analysis**, which processes the oscilloscope data in real time and performs fits to the cavity resonances.
- **2D raster scanning**, which generates real time 2D transmission images by scanning the cavity across the empty mirror or potentially the sample surface. In this case, an FPGA is interfaced between the PCIe card and detector to enable fast data acquisition and processing.

To enable full functionality of the Fluxi-GUI, additional hardware modifications were required. The piezo scanner tube possesses four electrodes, which enable 2D movement when opposing voltages are applied to opposite electrode pairs. As the program already creates the output voltages for both directions (but only one voltage polarity at a time), a voltage inverter was implemented to generate four control signals: two positive and two inverted signals, which is sufficient to establish lateral XY scanning. In order to fulfill the resonance condition, the cavity length is modulated in Z direction by applying an additional signal via a function generator. This modulation signal is combined with the lateral scanning signals using a voltage adder circuit. The resulting composite signal is then amplified before being applied to the piezo electrodes. This configuration enables full 3D control of the cavity fiber, allowing XY scanning for real time imaging and Z modulation to change the longitudinal mode order of the cavity.

5.3.3. Room temperature and cryogenic characterization

The first results were obtained by Fabian Heizmann, who commissioned the first iteration of this tube piezo cavity. Figure 5.3(a) shows the assembled cavity during operation, while Figure 5.3(b) highlights the internal view, illustrating the piezo scanner tube and the cavity fiber in front of the macroscopic planar mirror. At that time, fiber and mirror coatings were designed for operation in the red wavelength range around 640 nm, which are generally used for NV defect center experiments. The initial tests focused on characterizing the mechanical stability in the absence of active stabilization techniques.

The passive stability was evaluated by monitoring the drift of the cavity resonance over a time period of about 80 s, during which the cavity was modulated with a low voltage amplitude to isolate the fundamental mode. The resonance position was tracked over time, while the FWHM of the cavity linewidth was recorded simultaneously by the oscilloscope to enable the conversion into displacement units. During the measurement

⁴⁶ Model: BNC 2110, purchased from *National Instruments*.

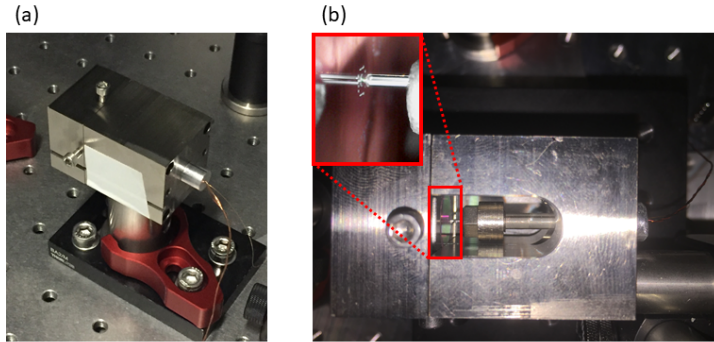


Figure 5.3: Visualization of the assembled cavity. (a) Image of the fiber-based cavity during its first successful operation, set up by **Fabian Heizmann**. (b) Inner view of the assembled cavity showing the mounted piezo scanner tube, including both the cavity fiber and the planar macroscopic mirror. The inset displays a zoomed-in image of the fiber glued into the needle opposing the cavity mirror.

period, a linear drift of 26 linewidths was observed, corresponding to an absolute displacement of 250 pm at a maximum observed finesse of $\approx 33\,000$. An FFT of the total resonance position and the multiplication with a displacement conversion factor yielded an amplitude spectral density of $0.79\text{ nm}/\sqrt{\text{Hz}}$ or a displacement of 3 pm s^{-1} . The linear drift behavior occurred rather randomly and may vary between different measurements. Assuming an integration bandwidth of $\Delta f = 1\text{ Hz}$ (0.01 Hz to 1 Hz), the resulting RMS displacement, in particular the cavity length jitter, is approximately 0.7 nm, demonstrating excellent passive stability at room temperature for an unstabilized system. In addition, it should be noted that this performance was achieved without any vibration isolation or acoustic shielding. The cavity was mounted directly on a cylindrical post, which was tightly fixed to the optical table. Compared to our other cavity systems, this observed passive stability is among the best at room temperature [141, 142], confirming the high mechanical robustness of the setup. With an active feedback loop, the system achieved a minimum RMS displacement of approximately 0.37 pm [141].

Both measurements indicated good stability, providing promising conditions for spectroscopic applications. To fully exploit the functionalities of the microcavity setup, the next step was to implement the scanning capability. In the following characterization measurements, the fiber coatings were changed to a center wavelength around 580 nm due to the future objective of investigating cavity-mediated effects on Eu^{3+} -based molecular systems.

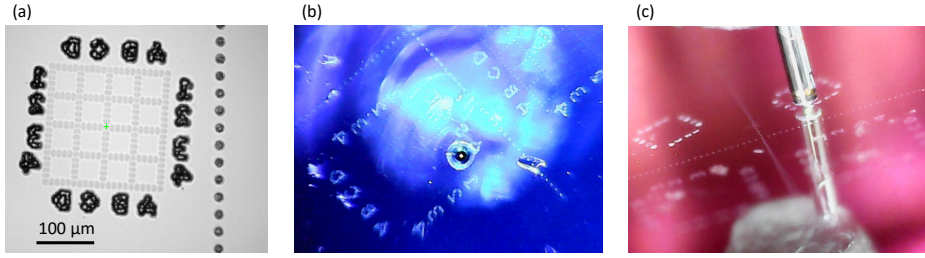


Figure 5.4: Marker grid reference structure used for alignment of the cavity for cooldown.

(a) Microscope image of the CO₂ laser-machined pattern on the mirror surface, where one square measures $50\ \mu\text{m} \times 50\ \mu\text{m}$. Typically, we shoot four marker grids on a single mirror, two of the latter dimensions and two with $100\ \mu\text{m} \times 100\ \mu\text{m}$ per square. (b) View of the marker grid and the fiber from behind the cavity. (c) Image from the alignment camera showing the marker grid used for positioning for the cooldown.

Preparation for cooldown: During the cooldown process, the primary goal was to determine the relative thermal drift of the cavity setup. In order to align the cavity for a cooldown, the lateral position and the cavity length must be adjusted. For this purpose, the cavity is positioned on a micrometer translation stage to coarsely bring the cavity fiber to an appropriate separation from the macroscopic mirror. The lateral position can be adjusted by using the fine-threaded alignment screws and a microscope camera to observe the movement of the mirror. As a visual reference, a chessboard-like pattern was laser-machined into the cavity mirrors employing our CO₂ laser, as depicted in Figure 5.4(a). Each square of this pattern typically measures $50\ \mu\text{m} \times 50\ \mu\text{m}$ (larger marker grids with $100\ \mu\text{m} \times 100\ \mu\text{m}$ are also available), which is well suited for the scanning range of the piezo tube. However, the piezo amplifier is configured for input voltages of $\pm 10\ \text{V}$, meaning that the full piezo scan range cannot be used, as a fraction of the total voltage is required for the Z modulation. Therefore, the objective during the cooldown preparation is to position the cavity fiber over a distinct corner or edge of the engraved pattern, as depicted in Figure 5.4(b) and (c). When a position is fixed, a final 2D transmission scan and a finesse measurement are performed, both of which are shown in Figure 5.5(a) and (b). A 2D transmission map is obtained by raster scanning the sample across the lateral XY directions, divided into a predefined number of pixels, with a cavity transmission spectrum recorded at each position. From each spectrum, either the maximum or average transmission signal is extracted to generate the final map. For a finesse measurement, the cavity length is modulated along the Z direction. The fundamental longitudinal modes are then fitted to extract both their spectral separation and FWHM, from which the finesse is calculated at the corresponding lateral XY position.

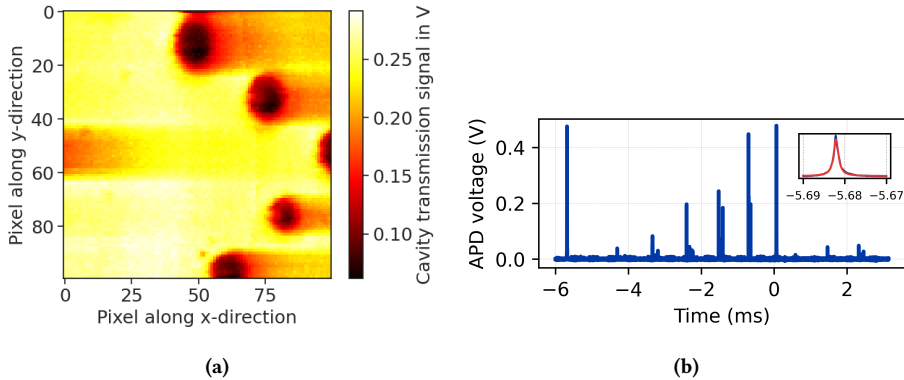
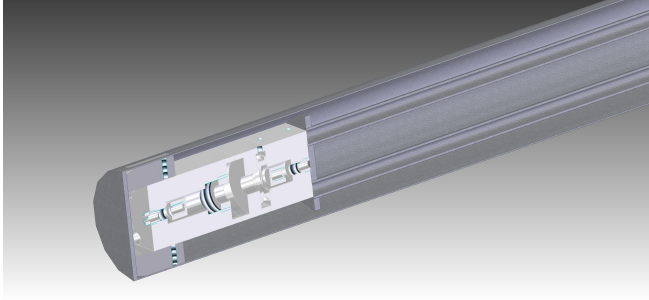


Figure 5.5: 2D transmission raster scan and finesse measurement. (a) 2D transmission raster scan over the marker grid pattern used for initial cavity alignment. Black dots represent either no transmission signal or a low transmission signal. (b) Finesse measurement with 580 nm laser light reveals sharp resonance peaks corresponding to a finesse of $\mathcal{F} \approx 4000$. The cavity angular alignment is not optimal, indicated by the higher-order transverse modes. The fit on the raw data is omitted for clarity, while the inset shows a zoomed-in view of a fitted resonance. In contrast, the finesse measurement for green light at 532 nm showed expected broader peaks, corresponding to a finesse of $\mathcal{F} \approx 80$.

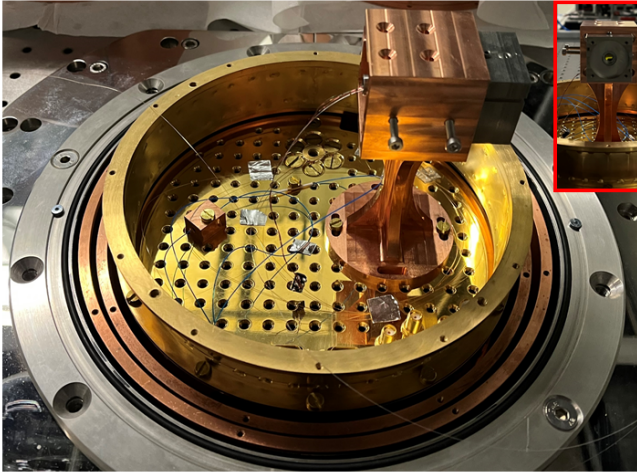
Cooldown in exchange gas dipstick and Sionludi cryostat: Upon cooldown, the cavity resonances begin to drift, as observed via the oscilloscope. To monitor this behavior, oscilloscope time traces were saved every 30 s throughout the entire cooldown process, enabling an approximate quantification of the drift in units of the FSR. Additionally, a 2D transmission scan was recorded at every 10 K temperature interval.

The experimental conditions were not ideal: the detector used was not designed for cryogenic operation, and the measurements were performed in a long, mechanically sensitive dipstick cryostat, which behaves like a resonator and is particularly susceptible to external vibrations. At room temperature, the cavity was aligned and tested in a horizontal configuration. During cooldown, however, it was operated in a vertical position, making it more prone to mechanical disturbances which potentially occurred during the transfer of the dipstick or when inserting it into the helium bath. For these reasons, the exchange gas dipstick proved to be an unsuitable cryogenic platform for stable cavity operation. The positioning of the assembled cavity inside the exchange gas dipstick cryostat is illustrated in the computer-aided design (CAD) cross-sectional view shown in Figure 5.6(a). Several cooldowns were performed, but only one yielded usable results, with a clear cavity resonance still visible at a temperature of 4.2 K. Reliable passive stability measurements could not be carried out under these conditions. Figure 5.7(a)–(f) show some recorded 2D transmission scans from room temperature down to 130 K. From then on, the scanning range was no longer sufficient to generate a 2D transmission image, as the piezo expansion significantly decreases at lower temperatures, which becomes evident by the reduction of the marker grid pattern size. It should be noted

5. Implementation of a new microcavity design for spectroscopy



(a)



(b)

Figure 5.6: Cavity integration into the cryostats. (a) CAD cross-sectional view showing the assembled cavity positioned within the exchange gas dipstick cryostat. The image was provided by **Michael Meyer** from the mechanical workshop of the *Physics Institute*. (b) Image of the copper mount incorporating the tube piezo cavity installed on the cold plate of the Sionludi cryostat. The inset displays the backside of the cavity, where the transmitted light is collected during the measurements.

that in addition to the cavity length changes, the lateral cavity positions also exhibit a slight drift toward the lower right.

Figure 5.7(g) and (h) display the first and final oscilloscope images taken during the entire cooldown, respectively. The analysis of all data indicated a relative drift of approximately $4\text{ }\mu\text{m}$ (≈ 14.5 FSR) over the full cooldown. This estimate is based on an assumed FSR of 266 nm ($\lambda/2$ for 532 nm), since the resonance drift was observed using green light, resulting in a lower cavity finesse. In this case, a lower finesse made the drift more easily observable due to broader resonance peaks. Interestingly, a reversed drift direction

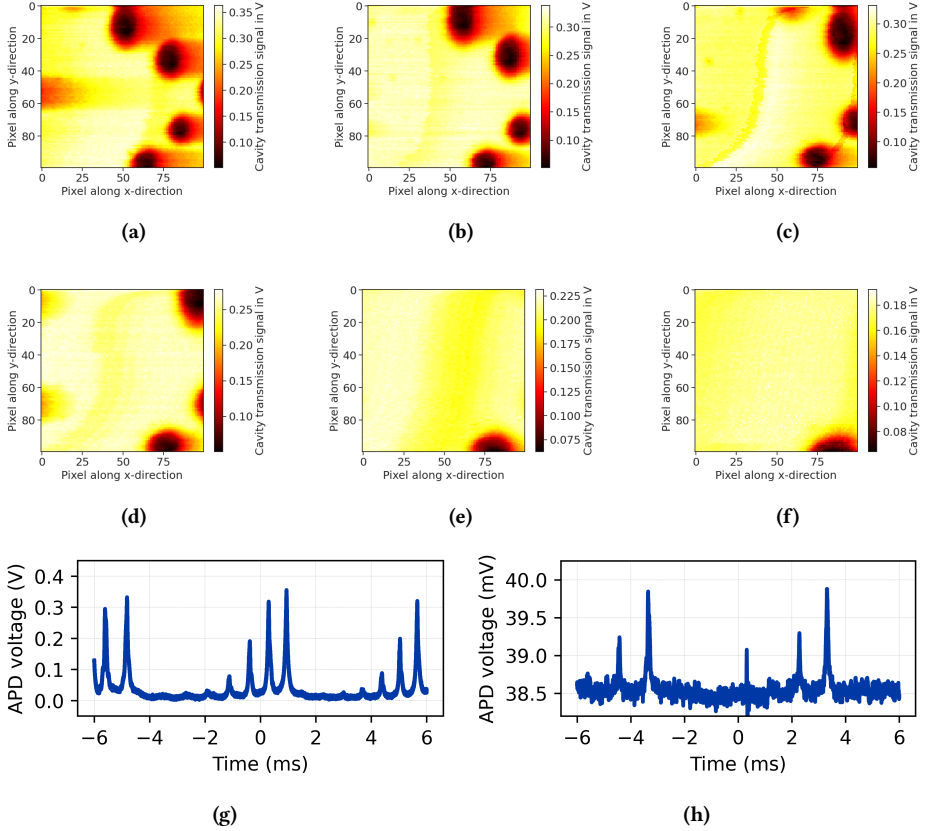


Figure 5.7: Measurements during a cooldown in the exchange gas dipstick. (a) 2D transmission scan of the marker grid at a temperature of $T = 280$ K. (b) $T = 250$ K. (c) $T = 220$ K. (d) $T = 190$ K. (e) $T = 150$ K. (f) $T = 130$ K. (g) and (h) denote the oscilloscope time traces at the beginning and the end of the cooldown. The analysis yielded a total drift in terms of the FSR of the fundamental cavity mode of about 14.5 (green light at 532 nm), corresponding to a relative shortening of $4\text{ }\mu\text{m}$ of the cavity length.

was observed below approximately 120 K. This behavior is likely caused by delayed contraction of the piezo, possibly due to insufficient thermal contacts at the epoxy joints. The full cooldown took approximately 6.5 h.

A similar measurement was repeated using the Sionludi cryostat, where a custom copper mount was fabricated to achieve thermalization of the cavity to the cold plate. Figure 5.6(b) illustrates the cavity inside the copper holder, which is installed inside the Sionludi cryostat. Again, the relative drift was monitored, resulting in a total shift of approximately 15 FSR of the fundamental mode (with higher uncertainty due to the rapid cooldown), which corresponds to a cavity length change of about $4\text{ }\mu\text{m}$ for 532 nm laser light. Although this value is consistent with the previous result in the

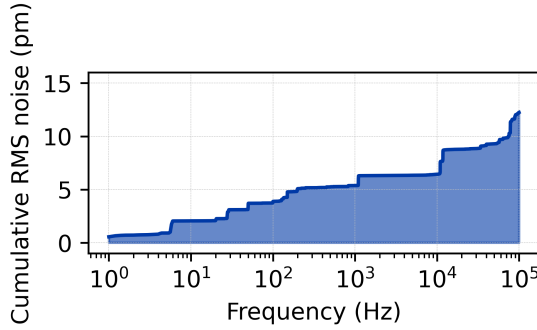


Figure 5.8: Measurement of the passive stability in the Sionludi cryostat. Passive stability measurement of the tube piezo cavity operated in the Sionludi cryostat. The cumulative RMS displacement is plotted as a function of the integration frequency bandwidth, yielding a total cavity length RMS jitter of about 12.25 pm, using red laser light at 640 nm and the side-of-fringe technique. This result confirms the excellent intrinsic mechanical stability of the system under cryogenic conditions. The measurement was performed at a temperature of about 100 mK.

dipstick cryostat, it carries significant uncertainty. Nevertheless, this method provides a preliminary estimate of the thermal drift behavior of the cavity setup. However, the 2D transmission scans were unsuccessful in this case due to a combination of fast cooldown (< 4 h) and an initially short cavity length, which caused the fiber to collide with the cavity mirror during thermal contraction. Toward the end of the cooldown, the cavity length increased again, likely due to delayed piezo contraction as in the previous case, leading to a retraction of the fiber from the cavity mirror. Although no 2D transmission scans could be acquired, a passive stability measurement was successfully carried out using the *side-of-fringe technique*, with the cavity being operated at a wavelength of 640 nm ($\mathcal{F} \approx 1700$). Red laser light was chosen for this measurement due to the broader resonance lines at this wavelength, which enable easier positioning on the resonance flank during the passive stability measurements. The cavity was biased to the slope of a resonance using a direct current battery, and a time trace of the transmitted signal was recorded. The resulting data showed an RMS displacement of 12.25 pm at a temperature of approximately 100 mK. Figure 5.8 represents the cumulative RMS value as a function of the integrated frequency bandwidth.

5.3.4. Conclusion of the cavity implementation

In conclusion, the cavity system has proven to be mechanically robust and promising. At room temperature, it fulfilled all expectations, demonstrating good passive stability, reliable scanning functionality, and sufficient scan range. Under cryogenic conditions, however, only a limited number of measurements could be performed, and a full characterization was not possible. This was due in part to limited time dedicated to cavity measurements and optimization processes, and in part to the lack of a more suitable cryostat beyond the mechanically unstable exchange gas dipstick cryostat.

Nevertheless, the promising passive stability of the cavity setup could be confirmed at low temperatures. To enable full scanning functionality under cryogenic conditions in future experiments, potential improvements could include the use of composite piezo designs, such as mounting a ring or stack piezo on top of the piezo tube, which would incorporate the fiber. This configuration could provide Z modulation of the cavity length, while the tube piezo continues to operate in the XY directions, thereby solving the issue of dividing the available voltage between these degrees of freedom. As a consequence, each actuator could operate to its full range, which may result in a usable scan range at millikelvin temperatures. It is clear that the setup has significant potential but will require further development and time investment to realize its full capabilities. Once membrane-like samples with well-controlled and reproducible preparation methods become achievable, the cavity system will also be suitable for initial cavity-mediated spectroscopic measurements at room temperature.

5.4. Outlook: toward cavity spectroscopy

As the development of the piezo cavity setup and spectroscopic investigations of Eu^{3+} -based molecular complexes progressed, initial attempts were already made to integrate molecular samples into a separate room temperature cavity. During my time as a Master's student, my work included first spectroscopic investigations of a diamond membrane within such a cavity. The technical details of this setup are documented in my Master's thesis [140].

A major challenge currently in cavity spectroscopy is the difficulty of preparing molecular samples directly on the cavity mirrors. Various methods, including spin coating and sublimation, were explored to create thin films. The molecular materials used in these attempts were SKR520 and BB3, respectively. Unfortunately, the results showed that at room temperature, the spectral linewidth of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ transition broadened by approximately one order of magnitude, indicating crystallization had not occurred and instead an amorphous medium had formed.

With the successful results arising from the recrystallization method, a new pathway was opened for growing crystalline molecular samples directly on the mirrors while preserving the exceptional optical properties. This approach was pursued by **Weizhe Li** in his Master's thesis, and initial spectroscopic measurements at room temperature were successfully performed on SKR520 [45].

A second approach was investigated by another Master's student, **Xiaoyu Yang**, who embedded the dinuclear complex BB3 in PMMA using spin coating, which produced a thin film of a thickness of approximately 300 nm. This sample was also used for preliminary spectroscopic measurements. However, the optical properties were significantly influenced, and the linewidth of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ transition was again broadened by roughly one order of magnitude [143].

These results clearly demonstrate that the integration of REI-based molecular samples into the cavity is not trivial, and each molecular compound possibly requires an individual preparation strategy. The overarching goal still remains to identify and establish a standardized and reproducible preparation method for the cavity integration. Nonetheless, we would like to conclude this chapter with an outlook on the first successful REI-based molecular spectroscopy measurements, based on the results obtained by Weizhe Li.

In order to perform spectroscopy of crystalline Eu^{3+} -based molecular samples, in particular SKR520, inside the cavity, a mirror-based recrystallization method is applied. The cavity mirror was partially submerged into a saturated solution, which formed a thin coating of the solution on the surface of the mirror due to capillary forces, as shown in Figure 5.9(a). Over the course of a week, the first successfully grown microcrystals were observed. The obtained mirror showed a clean surface with evenly distributed crystals, as demonstrated in Figure 5.9(b). After recrystallization, the mirror was imaged using

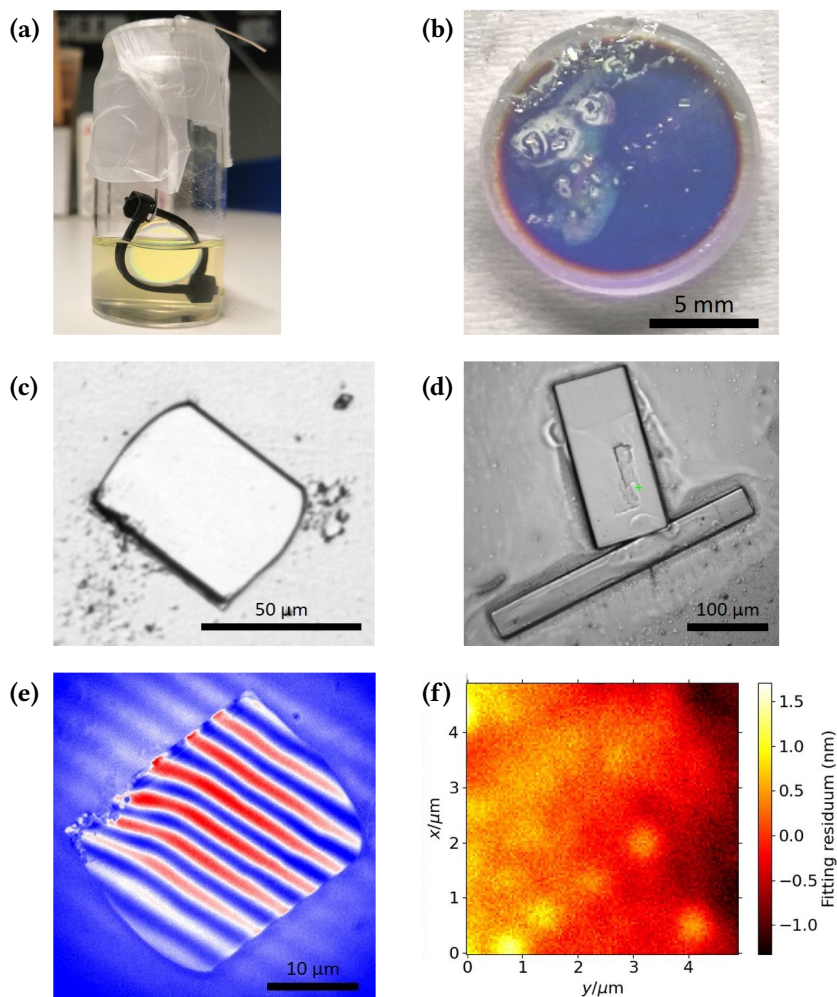


Figure 5.9: Cavity mirror recrystallization of SKR520 and WLI analysis. (a) The cavity mirror is hung halfway into the solution in order to initiate crystal growth. (b) Resulting mirror surface after successful recrystallization of SKR520, showing a homogeneous distribution of microcrystals. (c) and (d) illustrate two exemplary microcrystals grown on the mirror surface as observed under the microscope. The crystals exhibit a good RMS surface roughness and are spatially well-isolated from other microcrystals. (e) Interference pattern on the crystal shown in (c) measured with the WLI, indicating a smooth surface roughness. (f) Height profile obtained from WLI reconstruction. The profile is fitted to a plane, and the residuals are used to determine the surface roughness on an area of $5\ \mu\text{m} \times 5\ \mu\text{m}$, yielding a surface roughness of approximately $0.4\ \text{nm}$ RMS for the crystal in (c). Therefore, this microcrystal was used for most of the spectroscopic measurements. Scale bars indicate approximate sizes. All figures are taken from [45].

a microscope to examine the crystal distribution, and selected crystals, as depicted in Figure 5.9(c) and (d), were further characterized via our WLI. The interference pattern and the reconstructed height profile of the crystal shown in Figure 5.9(c) are presented in Figure 5.9(e) and (f), respectively. From the reconstructed topography, surface roughness values were extracted, yielding a promising RMS surface roughness of about 0.4 nm (the mirror surface roughness is at ≈ 0.2 nm RMS). The crystal thickness was determined to be approximately 2 μm . To confirm that the optical properties were preserved, confocal microscopy was then performed, revealing a well-defined emission line of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ transition with a linewidth of 0.017 nm, which is in good agreement with our observed and the reported values [1, 45].

When a crystalline material is introduced into a Fabry–Pérot cavity, as shown in Figure 5.10(a), the optical system becomes a hybrid cavity composed of two distinct regions: an air gap and a dielectric layer on the mirror. The electromagnetic field must satisfy boundary conditions at the air–dielectric material interface, leading to a coupling between the modes in both media. As a result, the cavity no longer supports independent air- or dielectric modes, but instead features hybridized modes that periodically transition between air-like and dielectric characteristics. This coupling results in a characteristic anti-crossing behavior in the mode dispersion, which is illustrated by the simulated dispersion (blue) in Figure 5.10(b) together with the individual pure air (orange) and dielectric modes (green). It can be seen that the hybridized modes avoid direct intersection when the wavelength is plotted as a function of the cavity length, or more specifically the air gap. This behavior reflects the fact that the hybrid system cannot be simultaneously resonant in both regions. The major characteristics of the individual modes are:

- **Air-like modes** are mostly confined in terms of energy to the air gap and exhibit steeper slopes (orange dashed lines).
- **Dielectric-like modes** have stronger field confinement in the dielectric medium (energy density higher due to refractive index: $n^2|E|^2$) and possess flatter slopes within the dispersion curves (green dashed lines).

The shape of these dispersion branches and the transmission of both modes depend on several factors, including the refractive index, the thickness of the dielectric medium, and the finesse differences between the air-like and dielectric-like cavities. We will not go into further detail here. More comprehensive explanations and considerations can be found in the work and publication of **Maximilian Pallmann** and **Jonathan Körber** [137, 142], respectively.

Figure 5.10(c) shows that the introduced microcrystal indeed forms a hybrid cavity, as confirmed by the measured mode dispersion using a broadband white-light laser source for excitation and a spectrometer for detection. The fundamental modes are clearly visible, while higher-order modes occasionally appear due to potential alignment variations. Figure 5.10(d) represents a zoomed-in view of a selected region of the full

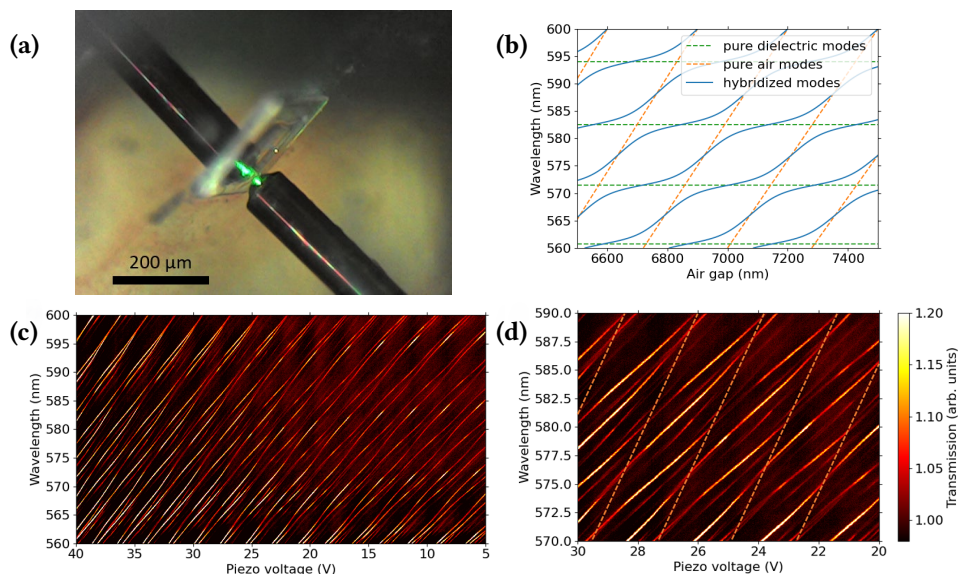


Figure 5.10: Measured mode dispersion of a hybrid cavity containing a molecular microcrystal. (a) Microscope image showing the fiber positioned above a crystallized region on the cavity mirror during an experiment with off-resonant excitation at 532 nm. Scale bar indicates approximate crystal sizes. (b) Simulated hybridized cavity modes (blue) in comparison with the pure air modes (orange dashed lines) and pure dielectric modes (green dashed lines). A hybridized mode appears air-like when it intersects a pure air mode, and dielectric-like when it intersects a pure dielectric mode. (c) Full broadband scan of the mode dispersion over a piezo voltage of 40 V, corresponding to a cavity length of 2 μm. (d) Zoomed-in view showing alternating air-like and dielectric-like modes. The steeper air-like modes exhibit a lower transmission, while the flatter dielectric-like modes feature a higher transmission, revealing clear mode hybridization. Orange dashed lines denote the reconstructed pure air modes. All pictures are taken from [45].

spectrum, offering a clearer visualization of the hybridization between air-like and dielectric-like modes. By analyzing the air-like modes, the underlying pure air modes can be reconstructed, from which an air gap of approximately 13 μm is extracted. The dielectric-like modes show a higher transmission, indicating a higher finesse of the dielectric cavity, which arises from the fact that mirror transmittance is altered when a dielectric-like mode occurs [45, 137].

In order to detect an initial signal from the Eu^{3+} ion ensemble within the recrystallized molecular sample, fluorescence spectroscopy was performed by employing the double resonance condition under 532 nm excitation, which requires both the excitation and emission wavelengths to coincide with the cavity resonances. The emitted fluorescence was detected by a spectrometer. A series of spectra was recorded at adjacent longitudinal mode orders of the cavity, meaning that the cavity length was stepwise changed, resulting

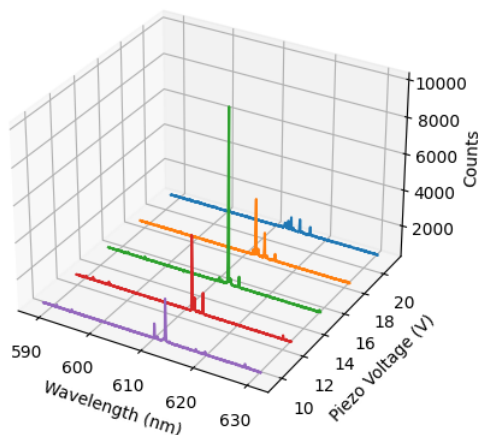


Figure 5.11: Cavity-mediated fluorescence measurements of SKR520. 3D plot showing fluorescence spectra recorded at different cavity lengths. The emission is significantly enhanced when the double resonance condition is fulfilled, as highlighted by the green spectrum. The figure is taken from [45].

in a 3D fluorescence waterfall plot, as shown in Figure 5.11. The emission is significantly increased since the double resonance condition is fulfilled, as emphasized by the green spectrum. This measurement demonstrates the successful detection of a cavity-mediated fluorescence signal from the Eu^{3+} -based molecular complex SKR520 [45].

During the ongoing ensemble spectroscopy efforts, it was encouraging to observe a first clear Eu^{3+} signal from the molecular sample within the cavity. This result, along with the complementary measurements performed by Xiaoyu Yang, represents an important step toward future cavity-based spectroscopy of REI-based molecular complexes and demonstrates the feasibility of integrating such materials into optical microcavities.

6. Summary and outlook

The emerging field of optically addressable, spin-bearing molecular systems is rapidly gaining attention and may soon complement well-established solid-state emitter platforms. Through chemical engineering, the ligand field surrounding the REIs can be precisely tailored, enabling targeted material properties. The diversity of chemical design strategies significantly facilitates this process. Before such molecular systems can be considered for integration into future scalable quantum information applications, several fundamental requirements must be fulfilled. This thesis contributes to this endeavor by presenting a comprehensive spectroscopic investigation of five Eu^{3+} -based molecular complexes. Among them, one reference sample (SKR520), previously characterized by our collaborators and reported in [1] served as a benchmark throughout the study.

The work involves not only extensive optical and spin characterization measurements, but also substantial setup development. Optical setups were refined, new pulse sequences were implemented, and sample integration techniques for various cryostats were developed. Because most samples were obtained as powders, we developed and improved a small-footprint, fiber-based ferrule sample holder compatible with all our dipstick cryostats based on previous work by **Xiaoyu Cheng** and **Christina Ioannou**. Initially, limited signal strength caused challenges due to suboptimal sample preparation. However, by adopting a new technique introduced by **Vishnu Unni C.**, which involved compressing the powder into the ferrule with a mini-spatula under a microscope, we achieved significantly higher optical depths and stronger absorption signals. In parallel, we adapted this holder for use in our dilution refrigerator, ensuring a robust thermal connection to the cold plate and thus enabling measurements in the millikelvin regime. A major advancement was the successful growth of macroscopic single crystals during the Master's thesis project of Vishnu Unni C.. Given the known advantages of bulk samples with respect to optical properties in crystalline materials over nano- or micro-sized particles, we also designed a modified sample holder in an asymmetric configuration to accommodate larger crystals and powder volumes. This enabled both free-space excitation and collection in the Sionludi cryostat and facilitated a direct comparison between powder-like and macroscopic geometries.

Spectroscopic methods played a central role in this work. Using the reference sample SKR520, we established a complete set of analysis procedures, including SHB, FID, and photon echo techniques. Optimized pulse sequences and parameters developed on this sample were systematically applied to all other molecular compounds, creating a standardized methodology.

Among the studied materials, first promising candidates emerged. All were investigated at a Eu^{3+} doping concentration of 100 %. Beyond the reference SKR520, which showed a relatively long optical coherence time of 10.5 μs , the fluorinated complexes BB1 and especially the dinuclear BB3 exhibited promising properties. BB3 demonstrated the highest branching ratio of 1.30 % of all examined materials and was the only sample where a photon echo was successfully measured, yielding an optical coherence time of 1.96 μs . While other samples also enabled narrow spectral holes and FID signals, photon echoes could not be observed, either due to insufficient optical depth or lack of optimized techniques at the time. The macroscopic crystal of SKR520 exhibited particularly favorable characteristics, including an inhomogeneous linewidth as narrow as 1.95 GHz, three times narrower than the previously reported value, and ultra-narrow spectral holes of 250 kHz. Although photon echoes could not be recorded for this crystal at the time due to limitations in our pulse sequence, these results underline its excellent material quality.

With respect to spin properties, all complexes showed long-lived hyperfine states, with characteristic lifetimes ranging from a few seconds up to several minutes. For example, SKR127 exhibited the longest hyperfine lifetime of 460 s. For SKR520, values approaching 5 min were consistent with the published results [1]. In general, all molecular complexes feature promising spin lifetimes, and most were found to be suitable for further exploration. To investigate their viability for quantum memory applications, which require long spin coherence times, we focused our nuclear spin characterization efforts on the reference sample. By extending our setup with a high-power amplifier and an *LC* resonator circuit with an integrated RF coil, we successfully demonstrated ODNMR on the 34 MHz hyperfine transition. Initial spin inhomogeneous linewidths were on the order of 230 kHz. Following additional optimizations and the transition to the macroscopic crystal within the asymmetric configuration of the sample holder, both hyperfine transitions (21.5 MHz and 34 MHz) could be probed. The 21.5 MHz transition exhibited a stronger oscillator strength under identical conditions and was selected for further measurements. Coherent nuclear spin control was demonstrated via Rabi oscillations, with Rabi frequencies of ~ 15 kHz at 120 W of RF power. A first spin coherence time of 613 μs was extracted, which was then extended to 2 ms using CPMG dynamical decoupling sequences to suppress dephasing from the surrounding proton spin bath of the hydrogen atoms. A preliminary $T_{2,s}^*$ of about 20 μs was estimated via spin hole burning measurements within the spin inhomogeneous line. A final key result was the observed correlation between spin and optical inhomogeneous linewidths, with an average spin-linewidth broadening factor of 18 kHz GHz^{-1} . These achievements mark the first complete nuclear spin characterization of a Eu^{3+} -based molecular system. Further confirmation and refinements are necessary. More stable decoupling sequences and a deeper analysis of the spin bath dephasing mechanisms would provide additional insights. This forms the basis for further investigations on similar REI-based molecular structures.

Moving forward, the hyperfine structure of new candidates must be determined. This requires high-quality, isotopically pure samples and detailed SHB measurements to

isolate side features from both isotopes and allow precise simulation-based fitting. Initial tests using the published SHB data have shown promising results for fitting and extracting the hyperfine levels.

If a suitable candidate is identified with regard to its intrinsic properties, the next logical step involves integration into a cryo-compatible optical cavity to enhance light-matter interaction. This is especially relevant for Eu^{3+} -based samples with low branching ratios and long excited-state lifetimes $T_{1,0}$. The main challenge is sample integration into the cavity while preserving the promising optical and spin properties. Initial approaches were explored in our research group by **Weizhe Li** and **Xiaoyu Yang** during their Master's theses, using recrystallization and PMMA embedding, respectively. Although both methods yielded first spectroscopic results within the cavity at room temperature, further optimization is required.

A robust and cryo-compatible cavity design was developed as part of this thesis and first set up by **Fabian Heizmann** during his Bachelor's thesis. Based on a piezo tube with XYZ scanning capability, the system is especially suitable for planar membrane samples. Room temperature characterizations show sub-picometer RMS passive stability and scanning ranges of $\sim 70\ \mu\text{m}$ in the X and Y directions. At low temperatures, including the millikelvin regime, the performance was reduced to about 12.25 pm RMS, mainly due to the vibrations introduced by the gas handling system of the cryostat. In addition, the 2D scanning capability was no longer available, since the piezo travel range at such cryogenic temperatures is low. The amplified voltage was sufficient to drive the piezo tube only in one direction. Future improvements may include stacked piezo solutions (ring piezo on tube piezo) to separate Z and X-Y voltage supply in order to provide scanning capabilities at cryogenic temperatures. Overall, this system represents a viable alternative to our conventional fiber-based microcavities, especially once reliable sample integration methods are reproducibly achieved.

As scientific work never stands still but expands with every new insight, we would like to conclude with a short outlook. Figures 6.1(a) and (b) present two newly synthesized asymmetric dinuclear molecular complexes that are already in our experimental pipeline. Both Eu^{3+} -based compounds, in contrast to BB3, potentially exhibit two spectrally separated inhomogeneous lines. Such dinuclear systems are particularly promising for realizing two-qubit platforms based on electric dipole-dipole interactions. The spectral separation of the Eu^{3+} ions simplifies individual addressing.

While the current RF setup demonstrated a clear proof of principle, several dephasing mechanisms still limit both optical and spin coherence times. Figure 6.1(c) also provides an outlook. So far only samples with 100 % Eu^{3+} doping concentration were used, which are susceptible to ion-ion interactions. First measurements on diluted Eu^{3+} samples with 50 % doping concentration reveal an optical coherence time of approximately 114 μs , which is nearly twice as long as the long-time component reported in [1], despite being measured at higher temperatures.

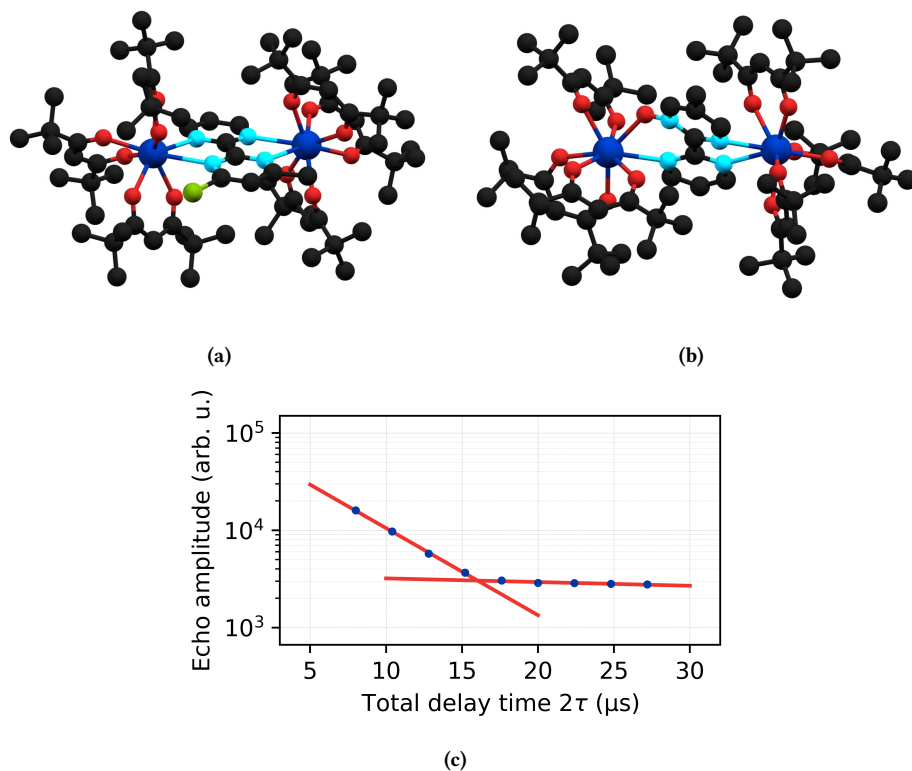


Figure 6.1: Outlook: Next steps in ensemble spectroscopy. (a) and (b) show two new dinuclear asymmetric molecular complexes that potentially exhibit two optical inhomogeneous lines arising from each optical center. These compounds constitute promising candidates for molecular two-qubit gates. Europium is shown in blue, oxygen in red, nitrogen in cyan, chloride in green, and carbon in black. Hydrogen is omitted for clarity. The molecular structures were provided by our collaborator **Dr. Barbora Brachnakova**. (c) Two-pulse photon echo measurement on a diluted SKR520 sample with a 50 % Eu^{3+} doping concentration, revealing two promising optical coherence times, both fitted with linear functions: $T_{2,o(\text{short})} = (4.86 \pm 0.10) \mu\text{s}$ and $T_{2,o(\text{long})} = (114 \pm 28) \mu\text{s}$. This effect was already observed in Ref. [1]. The measurement was performed at a temperature of 4.2 K.

Achieving spin coherence times beyond the current 2 ms range will likely require reaching the millikelvin regime. A new dilution refrigerator with an exchange gas chamber is already in the test phase, which should provide optimal thermalization of the sample. For RF applications in this system, new RF coupling methods such as coplanar waveguides may be required as RF powers on the order of 100 W are not compatible with the cooling power of the new cryostat. The work of **Ioannis Karapatzakis**, using coplanar waveguides deposited on a diamond membrane to coherently control electron spins in

SnV defect centers and coupled nearby ^{13}C nuclear spins, offers a possible strategy to circumvent high-power RF-driven coils and thus minimize thermal load [11].

Finally, this thesis has contributed significantly to the understanding of optically addressable, spin-bearing molecular systems and should serve as a basis for identifying and developing future candidates for quantum information applications. This field holds immense potential and is expected to attract more interest as more promising experimental findings emerge. With continued optimization of spectroscopic methods, improved and reproducible sample preparation, and integration into optical microcavities, the goal of scalable and applicable molecular quantum systems is definitely within reach.

Appendices

A. Overview of the ensemble spectroscopy pulse parameters

In this section, an overview of the pulse parameters used for various spectroscopic techniques is provided. Tables A.1 and A.2 briefly summarize the central parameters, including pulse durations, time delays, frequency detunings, and laser powers applied in individual optical or spin characterization experiments, in particular for SHB, FID, photon and spin echoes, ODNMR, and Rabi oscillations. These parameters were optimized individually depending on the sample and the measurement conditions and thus can differ in further experiments. However, they can serve as a reference for reproducing results or as a guideline for adapting measurements to new samples.

Table A.1: Pulse parameters for different optical spectroscopic techniques.

Spectroscopic technique	Pulse durations	Delay time	Frequency detuning or scan range	Optical power
SHB (narrow)	500 ms burn, 200 ms probe	50 ms to 200 ms	up to 80 MHz scan range	$\leq 500 \mu\text{W}$
SHB (wide)	2000 ms burn, 10 ms probe	50 ms to 100 ms	up to 160 MHz scan range	$\leq 500 \mu\text{W}$
FID	4 μs burn, 10 μs readout	~ 100 ns	30 MHz detuning of readout	up to 180 mW
Two-pulse photon echo	2 μs $\pi/2$ pulse, 2 μs π pulse, 2 μs readout	time evolution, steps of up to 1 μs	30 MHz detuning of readout	up to 180 mW
Three-pulse photon echo	2 μs $\pi/2$ pulses, 2 μs readout	time evolution, steps of up to 1 μs , t_w in steps of 0.5 μs	30 MHz detuning of readout	up to 180 mW

Table A.2: Pulse parameters for different spin spectroscopic techniques.

Spectroscopic technique	Pulse durations	Delay time/sequence details	Frequency/chirp rate	RF power
ODNMR (CW)	chirped measurement, 10 s burn, chirp according to chirp rate	composite pulse	50 kHz s^{-1} to 1000 kHz s^{-1}	0.2 W to 1 W
ODNMR (pointwise)	spectral pit preparation of widths up to 10 MHz in 200 ms burn pulses, 1 ms RF pulse, 1 ms to 2 ms readout	no pause between RF and readout pulses	steps of 10 kHz to 100 kHz	1 W to 120 W
Rabi oscillations	1 μs to 150 μs pulse widths	no pause between RF and readout pulses	resonance frequency of the respective hyperfine transition	20 W to 120 W
Spin echo	from Rabi measurement at distinct power level, here for SKR520: $\pi/2$ pulse of 18 μs , π pulse of 36 μs	in steps of 5 μs	resonance frequency of the respective hyperfine transition	$\sim 90 \text{ W}$
CPMG	same as for spin echo, only number of refocusing pulses changes: $\pi/2$ pulse of 18 μs , π pulse of 36 μs	in steps of 5 μs	resonance frequency of the respective hyperfine transition	$\sim 90 \text{ W}$
Spin hole burning (pointwise)	π pulse of 36 μs , for other powers, the π pulse must be adjusted according to the Rabi frequency	delay of less than 5 μs between the RF pulses and no delay time to the readout pulse	steps of 1 kHz to 2 kHz	$\sim 90 \text{ W}$

B. Details on the coil geometry and the calculation of the magnetic field

This section presents the geometries and characteristics of the RF coils used for nuclear spin manipulation. Each coil was characterized by measuring its reflection spectrum, and the resulting data were fitted using a Fano resonance model to accurately extract the width of the coil resonance. The measured resonance frequencies and the corresponding coils are illustrated in Figure B.1. These measurements allow for a precise estimation of the coil performance at the operating frequencies.

Based on the coil dimensions, the magnetic field strength B at the sample position is estimated, with the results and the corresponding parameters presented in Table B.3. These values are particularly essential for determining the expected Rabi frequencies and for evaluating the efficiency of nuclear spin control in the reference sample SKR520. It must be noted that the expected values for the Rabi frequency deviate from the observed results, indicating approximations in the estimation model. This discrepancy is likely due to the gyromagnetic ratio being an anisotropic quantity, combined with the random alignment of the magnetic field relative to the average magnetic moment. The gyromagnetic ratio used in the calculation corresponds to $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ [55]. However, the measurements were performed on a Eu^{3+} -based molecular complex, for which this parameter has not been specifically determined.

Table B.3: Parameters used to estimate the magnetic field strength B for both coils.

Parameter	Coil 1	Coil 2
Number of turns N	27	62
Inner diameter d_{in} (mm)	1.25	2.55
Outer diameter d_{out} (mm)	2.15	3.45
Length l (cm)	1.7	2
Current I (A) for $R = 150 \, \Omega$ and maximum RF power of 150 W	1.73	1.73
Resonance frequency f (MHz)	34	21.5
Quality factor Q	22.5	10.75
Magnetic field B (mT)	3.384	6.454
Rabi frequency Ω_R (kHz) for $\gamma \sim 10 \, \text{MHz T}^{-1}$ [144]	33.84	64.54

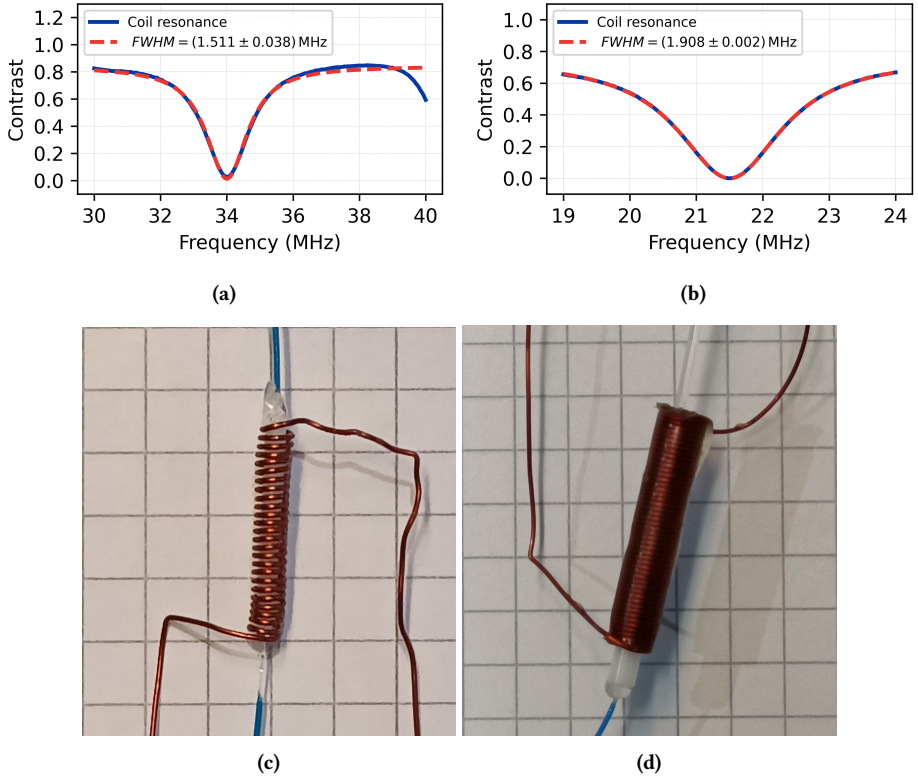


Figure B.1: Resonance characterization of the RF coils. (a) and (b) show the reflection spectra of both RF coils used within this work, each fitted with a Fano resonance to extract their linewidth. The resulting linewidths are presented in the legends. The first coil was only used to probe the 34 MHz hyperfine transition, while the second coil was employed for both transitions. The resonance shown in (b) here is tuned to 21.5 MHz. (c) and (d) are photographs of the corresponding RF coil geometries placed on centimeter-scaled paper for clearer visualization. The first coil exhibits spacings between the windings, while the second coil is more compact with no spacing between the windings, as it is encapsulated with a two-component epoxy adhesive.

C. Cross-sectional view of the Sionludi

In order to provide a clearer understanding of the setup, a cross-sectional view of the Sionludi cryostat is shown in Figure C.2. Additional technical details are described in the corresponding caption.

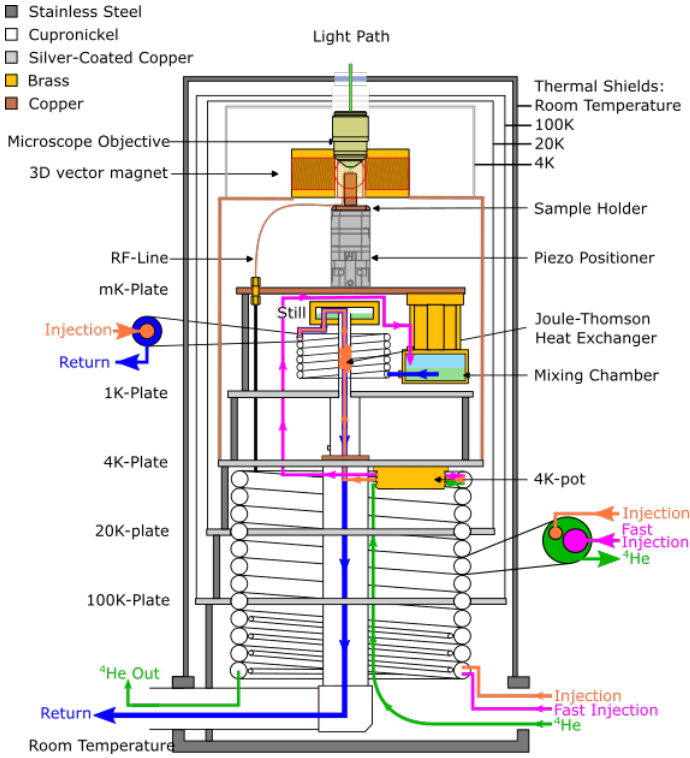


Figure C.2: Cross-section of the Sionludi dilution refrigerator. The diagram highlights the thermal architecture, including four radiation shields (from room temperature down to 4 K) and five temperature stages (100 K, 20 K, 4 K, 1 K, and mK-plate). The color-coded lines represent the flow paths of the two cooling circuits: the precooling of the cryostat is achieved via liquid ^4He (green). The respective transfer tube incorporates two additional lines, the injection (orange) and the fast injection (magenta), which belong to the $^3\text{He}/^4\text{He}$ dilution loop. The loop construction was designed to ensure that the returning helium precools the incoming $^3\text{He}/^4\text{He}$ mixture via the counterflow heat-exchange principle. The return path of the $^3\text{He}/^4\text{He}$ mixture is shown in blue. The injection and fast injection lines are directly connected to the mixing chamber. Further technical details can be found in the work of Alexander Zilz [104]. The figure is taken from [145, 11].

D. Abbreviations

QIP	quantum information processing
NV	nitrogen-vacancy
SiV	silicon-vacancy
SnV	tin-vacancy
GeV	germanium-vacancy
SnV	tin-vacancy
PbV	lead-vacancy
ZPL	zero-phonon line
QDs	quantum dots
REI	Rare-earth ion
REIs	Rare-earth ions
AFC	Atomic Frequency Comb
ZEFOZ	ZEro First-Order Zeeman
SQUARE	Scalable Rare-Earth Quantum Computing Nodes
SBCT	symmetry breaking charge transfer
TM	transition metals
EPR	electron paramagnetic resonance
ISC	intersystem crossing
RF	radio frequency
NMR	nuclear magnetic resonance
CF	crystal field
FWHM	full width at half maximum
TLS	two-level system

TLSs	two-level systems
LFM	low-frequency vibrational mode
LFMs	low-frequency vibrational modes
ISD	instantaneous spectral diffusion
QEC	Quantum error correction
CNOT	Controlled-NOT
MW	microwave
SECHYP	secant hyperbolicus
NISQ	Noisy Intermediate-Scale Quantum
DAQ	data acquisition
PDH	Pound–Drever–Hall
RMS	root mean square
FSR	free spectral range
BiFi	birefringent filter
EOM	electro-optic modulator
GUI	graphical user interface
PBS	polarizing beam splitter
OSA	optical spectrum analyzer
AOM	acousto-optic modulator
HWP	half-wave plate
APD	avalanche photodiode
AWG	arbitrary waveform generator
IQ	in-phase and quadrature
FPGA	field-programmable gate array
PPU	pulse processing unit

DACs	Digital-to-analog converters
ADCs	Analog-to-digital converters
QWP	quarter-wave plate
SMA	SubMiniature version A
NA	numerical aperture
VNA	vector network analyzer
PMMA	poly(methyl methacrylate)
WLI	white-light interferometer
MR	multiphonon relaxation
PL	photoluminescence
SHB	spectral hole burning
FID	free-induction decay
PLE	photoluminescence excitation
ODNMR	optically detected nuclear magnetic resonance
CPMG	Carr–Purcell–Meiboom–Gill
CW	continuous-wave
FFT	fast Fourier transform
SNR	signal-to-noise ratio
ROC	Radius of curvature
cQED	Cavity quantum electrodynamics
DBR	distributed Bragg reflector
SiPM	silicon photomultiplier
PCIe	Peripheral Component Interconnect Express
BNC	Bayonet Neill–Concelman
CAD	computer-aided design

E. Publications and conference contributions

Publications

- *"Observation of Narrow Optical Homogeneous Linewidth and Long Nuclear Spin Lifetimes in a Prototypical [Eu(trensal)] Complex"*
S.K. Kuppusamy, E. Vasilenko, W. Li, J. Hessenauer, C. Ioannou, O. Fuhr, D. Hunger, and M. Ruben
J. Phys. Chem. C 2023, 127, 10670-10679, published May 23, 2023,
DOI: <https://pubs.acs.org/doi/pdf/10.1021/acs.jpcc.3c02903>
- *"Scanning Cavity Microscopy of a Single-Crystal Diamond"*
J. Körber, M. Pallmann, J. Heupel, R. Stöhr, E. Vasilenko, T. Hümmer, L. Kohler, C. Popov, and D. Hunger
Phys. Rev. Applied 19, 064057, published June 20, 2023,
DOI: <https://doi.org/10.1103/PhysRevApplied.19.064057> (with published erratum)
- *"Spectral Hole-Burning Studies of a Mononuclear Eu(III) Complex Reveal Narrow Optical Linewidths of the $^5D_0 \rightarrow ^7F_0$ Transition and Seconds Long Nuclear Spin Lifetimes"*
S. Schlittenhardt, E. Vasilenko, V. Unni C., N.L. Jobbitt, O. Fuhr, D. Hunger, M. Ruben, and S.K. Kuppusamy
ChemPhysChem, Volume 25, Issue 19, published June 18, 2024,
DOI: <https://doi.org/10.1002/cphc.202400280>
- *"Optically detected nuclear magnetic resonance of coherent spins in a molecular complex"*
E. Vasilenko, V. Unni C., J. Resch, N.L. Jobbitt, D. Serrano, P. Goldner, S.K. Kuppusamy, M. Ruben, and D. Hunger
Nature Materials (2026), published March 19, 2026,
DOI: <https://doi.org/10.1038/s41563-026-02539-0>
- *"Controlled ion-ion interactions and cavity-enhanced emission of a coherent dinuclear Eu^{3+} complex"*
E. Vasilenko, V. Unni C., B. Brachnakova, N.L. Jobbitt, S.K. Kuppusamy, D. Hunger, and M. Ruben
Manuscript submitted (April 2026)

Conference contributions

- *"Development of a coherent spin-photon interface for quantum repeaters using NV centers in diamond"*
DPG-Tagung der Sektion AMOP, Poster
Rostock, Germany, March 2019
- *"Fully fiber-coupled devices for efficient cryogenic spectroscopy of single and small ensembles of rare-earth ions"*
DPG-Tagung der Sektion AMOP, Poster
Online conference, March 2021
- *"Fully fiber-coupled devices for efficient cryogenic spectroscopy of single and small ensembles of rare-earth ions"*
718. WE-Heraeus-Seminar, Poster (shared)
Bad Honnef, Germany, August 2021
- *"A fully fiber-coupled cavity for efficient cryogenic spectroscopy of molecular quantum emitters"*
Karlsruhe Days of Optics & Photonics, Poster
Online conference, Germany, November 2021
- *"Cavity-enhanced spectroscopy of molecular quantum emitters"*
DPG-Tagung der Sektion AMOP, Poster
Online conference, March 2022
- *"Cavity-enhanced spectroscopy of molecular quantum emitters"*
REI workshop 2022, Poster
Edinburgh, Scotland, July 2022
- *"Cavity-enhanced spectroscopy of molecular quantum emitters"*
DPG-Tagung der Sektion KM, Poster
Regensburg, Germany, September 2022
- *"Ensemble spectroscopy of molecular quantum emitters"*
Karlsruhe School of Optics & Photonics Summer School, Poster
Bad Herrenalb, Germany, September 2022
- *"Cavity-enhanced spectroscopy of molecular quantum emitters"*
DPG-Tagung der Sektion AMOP, Poster
Hannover, Germany, March 2023
- *"Spectroscopy and cavity-enhanced emission of Europium-based solid-state and molecular systems"*
REI workshop 2023, Talk (shared)
Lund, Sweden, September 2023

-
- *"Ensemble spectroscopy of Eu-based molecular quantum emitters"*
Karlsruhe Days of Optics & Photonics, Poster
Karlsruhe, Germany, November 2023
 - *"Ensemble spectroscopy and cavity-coupled emission of Eu-based molecular systems"*
DPG-Tagung der Sektion AMOP, Talk
Freiburg, Germany, March 2024
 - *"Spectroscopy and cavity-coupled emission of Europium-based molecular systems"*
QUANTUMatter 2024 conference, Poster
San Sebastian, Spain, May 2024
 - *"Spectroscopy and cavity-coupled emission of Europium-based molecular systems"*
Karlsruhe School of Optics & Photonics Summer School, Poster
Bad Herrenalb, Germany, September 2024

Bibliography

- [1] D. Serrano, S. K. Kuppasamy, B. Heinrich, O. Fuhr, D. Hunger, M. Ruben, and P. Goldner, “Ultra-narrow optical linewidths in rare-earth molecular crystals,” *Nature*, vol. 603, pp. 241–246, 2022.
- [2] Nature Editorial, “How quantum mechanics emerged in a few revolutionary months 100 years ago,” *Nature*, vol. 637, pp. 269–271, January 2025. Essay.
- [3] D. P. DiVincenzo, “The Physical Implementation of Quantum Computation,” *Fortschritte der Physik*, vol. 48, no. 9–11, pp. 771–783, 2000.
- [4] R. P. Feynman, “Simulating Physics with Computers,” *International Journal of Theoretical Physics*, vol. 21, no. 6, pp. 467–488, 1982.
- [5] IBM, “What Is Quantum Computing?.” <https://www.ibm.com/think/topics/quantum-computing>, 2024. Accessed: 2025-05-16.
- [6] R. Blatt and D. J. Wineland, “Entangled states of trapped atomic ions,” *Nature*, vol. 453, pp. 1008–1015, 2008.
- [7] J. J. Bollinger, D. J. Heinzen, W. M. Itano, S. L. Gilbert, and D. J. Wineland, “A 303-MHz Frequency Standard Based on Trapped $^9\text{Be}^+$ Ions,” *IEEE Transactions on Instrumentation and Measurement*, vol. 40, no. 2, pp. 126–128, 1991.
- [8] P. T. H. Fisk, M. J. Sellars, M. A. Lawn, C. Coles, A. G. Mann, and D. G. Blair, “Very high Q microwave spectroscopy on trapped $^{171}\text{Yb}^+$ ions: application as a frequency standard,” *IEEE Transactions on Instrumentation and Measurement*, vol. 44, no. 2, pp. 113–116, 1995.
- [9] G. Pieplow, C. G. Torun, J. H. D. Munns, F. M. Herrmann, A. Thies, T. Pregnolato, and T. Schröder, “Quantum Electrometer for Time-Resolved Material Science at the Atomic Lattice Scale,” *arXiv preprint arXiv:2401.14290*, 2024.
- [10] L. D. Santis, M. E. Trusheim, K. C. Chen, and D. R. Englund, “Investigation of the Stark Effect on a Centrosymmetric Quantum Emitter in Diamond,” *Physical Review Letters*, vol. 127, no. 14, p. 147402, 2021.
- [11] I. Karapatzakis, *Microwave Control of the Tin-Vacancy Spin Qubit in Diamond with a Superconducting Waveguide*. Phd thesis, Karlsruhe Institute of Technology,

Karlsruhe, Germany, 2025.

- [12] D. D. Sukachev, A. Sipahigil, C. T. Nguyen, M. K. Bhaskar, R. E. Evans, F. Jelezko, and M. D. Lukin, “Silicon-Vacancy Spin Qubit in Diamond: A Quantum Memory Exceeding 10 ms with Single-Shot State Readout,” *Physical Review Letters*, vol. 119, no. 22, p. 223602, 2017.
- [13] A. Faraon, P. E. Barclay, C. Santori, K.-M. C. Fu, and R. G. Beausoleil, “Resonant enhancement of the zero-phonon emission from a colour centre in a diamond cavity,” *Nature Photonics*, vol. 5, pp. 301–305, 2011.
- [14] T. Iwasaki, Y. Miyamoto, T. Taniguchi, P. Siyushev, M. H. Metsch, F. Jelezko, and M. Hatano, “Tin-Vacancy Quantum Emitters in Diamond,” *Physical Review Letters*, vol. 119, no. 25, p. 253601, 2017.
- [15] A. J. Shields, “Semiconductor quantum light sources,” *Nature Photonics*, vol. 1, pp. 215–223, 2007.
- [16] R. J. Warburton, “Self-assembled semiconductor quantum dots,” *Contemporary Physics*, vol. 43, no. 5, pp. 351–364, 2002.
- [17] R. J. Warburton, “Single spins in self-assembled quantum dots,” *Nature Materials*, vol. 12, pp. 483–493, 2013.
- [18] R. W. Equall, Y. Sun, R. L. Cone, and R. M. Macfarlane, “Ultraslow Optical Dephasing in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$,” *Physical Review Letters*, vol. 72, no. 14, pp. 2179–2182, 1994.
- [19] Y. Sun, C. W. Thiel, R. L. Cone, R. W. Equall, and R. L. Hutcheson, “Recent Progress in Developing New Rare Earth Materials for Hole Burning and Coherent Transient Applications,” *Journal of Luminescence*, vol. 98, no. 1, pp. 281–287, 2002.
- [20] M. Zhong, M. P. Hedges, R. L. Ahlfeldt, J. G. Bartholomew, S. E. Beavan, S. M. Wittig, J. J. Longdell, and M. J. Sellars, “Optically addressable nuclear spins in a solid with a six-hour coherence time,” *Nature*, vol. 517, no. 7533, pp. 177–180, 2015.
- [21] F. Wang, M. Ren, W. Sun, M. Guo, M. J. Sellars, R. L. Ahlfeldt, J. G. Bartholomew, J. Yao, S. Liu, and M. Zhong, “Nuclear Spins in a Solid Exceeding 10-Hour Coherence Times for Ultra-Long-Term Quantum Storage,” *PRX Quantum*, vol. 6, p. 010302, 2025.
- [22] M. Nilsson and S. Kröll, “Solid state quantum memory using complete absorption and re-emission of photons by tailored and externally controlled inhomogeneous absorption profiles,” *Optics Communications*, vol. 247, no. 4–6, pp. 393–403, 2005.

-
- [23] B. Kraus, W. Tittel, N. Gisin, M. Nilsson, S. Kröll, and J. I. Cirac, “Quantum Memory for Nonstationary Light Fields Based on Controlled Reversible Inhomogeneous Broadening,” *Physical Review A*, vol. 73, no. 2, p. 020302, 2006.
- [24] M. P. Hedges, J. J. Longdell, Y. Li, and M. J. Sellars, “Efficient Quantum Memory for Light,” *Nature*, vol. 465, pp. 1052–1056, 2010.
- [25] M. Afzelius, C. Simon, H. de Riedmatten, and N. Gisin, “Multimode Quantum Memory Based on Atomic Frequency Combs,” *Physical Review A*, vol. 79, no. 5, p. 052329, 2009.
- [26] H. de Riedmatten, M. Afzelius, M. U. Staudt, C. Simon, and N. Gisin, “A Solid-State Light–Matter Interface at the Single-Photon Level,” *Nature*, vol. 456, no. 7223, pp. 773–777, 2008.
- [27] I. Usmani, M. Afzelius, H. de Riedmatten, and N. Gisin, “Mapping Multiple Photonic Qubits into and out of One Solid-State Atomic Ensemble,” *Nature Communications*, vol. 1, p. 12, 2010.
- [28] N. L. Jobbitt, *Laser site-selective spectroscopy, Zeeman spectroscopy and crystal-field analysis of yttrium orthosilicate doped with Sm^{3+} and Er^{3+} ions*. Phd thesis, University of Canterbury, Christchurch, New Zealand, 2021.
- [29] S. Welinski, A. Tiranov, M. Businger, A. Ferrier, M. Afzelius, and P. Goldner, “Coherence Time Extension by Large-Scale Optical Spin Polarization in a Rare-Earth Doped Crystal,” *Physical Review X*, vol. 10, no. 3, p. 031060, 2020.
- [30] J. V. Rakonjac, Y.-H. Chen, S. P. Horvath, and J. J. Longdell, “Long Spin Coherence Times in the Ground State and in an Optically Excited State of $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ at Zero Magnetic Field,” *Physical Review B*, vol. 101, no. 18, p. 184430, 2020.
- [31] A. Ulanowski, J. Früh, F. Salamon, A. Holzäpfel, and A. Reiserer, “Spectral Multiplexing of Rare-Earth Emitters in a Co-Doped Crystalline Membrane,” *Advanced Optical Materials*, vol. 12, no. 15, p. 2302897, 2024.
- [32] R. L. Ahlefeldt, M. J. Pearce, M. R. Hush, and M. J. Sellars, “Quantum Processing with Ensembles of Rare-Earth Ions in a Stoichiometric Crystal,” *Physical Review A*, vol. 101, no. 1, p. 012309, 2020.
- [33] A. Kinoshita, D. Hunger, R. Kolesov, K. Mølmer, H. de Riedmatten, P. Goldner, A. Tal-laire, L. Morvan, P. Berger, S. Welinski, K. Karrai, L. Rippe, S. Kröll, and A. Walther, “Roadmap for Rare-earth Quantum Computing,” *arXiv*, 2021.
- [34] T. Eichhorn, *Cavity-enhanced Spectroscopy of Individual Europium-doped Nanoparticles*. Phd thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2024.

- [35] S. K. Kuppusamy, D. Hunger, M. Ruben, P. Goldner, and D. Serrano, "Spin-bearing molecules as optically addressable platforms for quantum technologies," *Nanophotonics*, vol. 13, no. 24, pp. 4357–4379, 2024.
- [36] M. S. Fataftah and D. E. Freedman, "Progress towards creating optically addressable molecular qubits," *Chemical Communications*, vol. 54, no. 98, pp. 13773–13781, 2018.
- [37] S. K. Kuppusamy, E. Vasilenko, W. Li, J. Hessenauer, C. Ioannou, O. Fuhr, D. Hunger, and M. Ruben, "Observation of Narrow Optical Homogeneous Linewidth and Nuclear Spin Lifetimes in a Prototypical [Eu(trensal)] Complex," *The Journal of Physical Chemistry C*, vol. 127, no. 22, pp. 10670–10679, 2023.
- [38] S. L. Bayliss, P. Deb, D. W. Laorenza, M. Onizhuk, G. Galli, D. E. Freedman, and D. D. Awschalom, "Enhancing Spin Coherence in Optically Addressable Molecular Qubits through Host-Matrix Control," *Physical Review X*, vol. 12, p. 031028, August 2022.
- [39] D. R. P. Jr., A. Prabhu, S. Tobar, J. D'Amelio, A. Tram, Z. W. Riedel, D. P. Shoemaker, and E. A. Goldschmidt, "Narrow optical linewidths in stoichiometric layered rare-earth crystals," *arXiv preprint arXiv:2411.02683*, 2024.
- [40] O. E. Mor, T. Ohana, A. Borne, Y. Diskin-Posner, M. Asher, O. Yaffe, A. Shanzer, and B. Dayan, "Tapered Optical Fibers Coated with Rare-Earth Complexes for Quantum Applications," *ACS Photonics*, vol. 9, no. 8, pp. 2676–2682, 2022.
- [41] B. G. Wybourne, *Spectroscopic Properties of Rare Earths*. New York: Interscience Publishers, 1965.
- [42] A. J. Freeman and R. E. Watson, "Theoretical Investigation of Some Magnetic and Spectroscopic Properties of Rare-Earth Ions," *Physical Review*, vol. 127, no. 6, pp. 2058–2075, 1962.
- [43] D. L. Clark, "The Chemical Complexities of Plutonium," *Los Alamos Science*, no. 26, pp. 364–381, 2000.
- [44] J. J. Longdell, *Quantum Information Processing in Rare Earth Ion Doped Insulators*. Phd thesis, The Australian National University, 2003.
- [45] W. Li, "Cavity-Enhanced Spectroscopy of Molecular Rare-earth-ion Complex," master's thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2023.
- [46] P. Goldner, A. Ferrier, and O. Guillot-Noël, "Rare Earth-Doped Crystals for Quantum Information Processing," in *Handbook on the Physics and Chemistry of Rare Earths* (J.-C. G. Bünzli and V. K. Pecharsky, eds.), vol. 46, pp. 1–78, North Holland, 2015.

-
- [47] G. H. Dieke and H. M. Crosswhite, "The Spectra of the Doubly and Triply Ionized Rare Earths," *Applied Optics*, vol. 2, no. 7, pp. 675–686, 1963.
- [48] K. Binnemans, "Interpretation of europium(III) spectra," *Coordination Chemistry Reviews*, vol. 295, pp. 1–45, 2015.
- [49] G. Liu and B. Jacquier, *Spectroscopic Properties of Rare Earths in Optical Materials*. Springer Berlin, Heidelberg, 2005.
- [50] R. M. Macfarlane and R. M. Shelby, "Coherent Transient and Holeburning Spectroscopy of Rare Earth Ions in Solids," in *Spectroscopy of Solids Containing Rare Earth Ions* (A. A. Kaplyanskii and R. M. Macfarlane, eds.), pp. 51–184, Amsterdam: North-Holland, 1987.
- [51] W. T. Carnall, G. L. Goodman, K. Rajnak, and R. S. Rana, "A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3 ," *The Journal of Chemical Physics*, vol. 90, no. 7, pp. 3443–3457, 1989.
- [52] B. R. Judd and J. A. White, "Operator Techniques in Atomic Spectroscopy," *Physics Today*, vol. 17, no. 4, p. 72, 1964.
- [53] M. Weissbluth, *Atoms and Molecules*. Academic Press, 1978.
- [54] R. D. Cowan, *The Theory of Atomic Structure and Spectra*, vol. 3 of *Los Alamos Series in Basic and Applied Sciences*. University of California Press, 1981.
- [55] J. J. Longdell, A. L. Alexander, and M. J. Sellars, "Characterization of the Hyperfine Interaction in Europium-Doped Yttrium Orthosilicate and Europium Chloride Hexahydrate," *Physical Review B*, vol. 74, no. 19, p. 195101, 2006.
- [56] W. Demtröder, *Laser Spectroscopy 1*. Springer Berlin, Heidelberg, 2014.
- [57] C. Ioannou, "Ensemble spectroscopy of novel europium doped materials for quantum information processing," master's thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2022.
- [58] R. S. Meltzer and K. S. Hong, "Electron-phonon interactions in insulating nanoparticles: Eu_2O_3 ," *Physical Review B*, vol. 61, no. 5, pp. 3396–3403, 2000.
- [59] D. E. McCumber and M. D. Sturge, "Linewidth and Temperature Shift of the R Lines in Ruby," *Journal of Applied Physics*, vol. 34, no. 6, pp. 1682–1684, 1963.
- [60] Y. G. Vainer, A. V. Naumov, and L. Kador, "Local vibrations in disordered solids studied via single-molecule spectroscopy: Comparison with neutron, nuclear, Raman scattering, and photon echo data," *Physical Review B*, vol. 77, no. 22, p. 224202, 2008.

- [61] B. Kozankiewicz and M. Orrit, "Single-molecule photophysics, from cryogenic to ambient conditions," *Chemical Society Reviews*, vol. 43, no. 4, pp. 1029–1043, 2014.
- [62] V. U. Chorakkunnath, "Coherent Spectroscopy of Molecular Rare-Earth-Ion Complexes," master's thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2023.
- [63] P. W. Anderson, B. I. Halperin, and C. M. Varma, "Anomalous low-temperature thermal properties of glasses and spin glasses," *Philosophical Magazine*, vol. 25, no. 1, pp. 1–9, 1972.
- [64] J. G. Bartholomew, K. de Oliveira Lima, A. Ferrier, and P. Goldner, "Optical Line Width Broadening Mechanisms at the 10 kHz Level in $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ Nanoparticles," *Nano Letters*, vol. 17, no. 2, pp. 778–787, 2017.
- [65] W. van Weperen and H. W. de Hartog, "Electric dipoles in rare-earth-doped SrF_2 : Relaxation parameters and dipole-dipole interaction," *Physical Review B*, vol. 18, no. 6, pp. 2857–2865, 1978.
- [66] D. L. Orth, R. J. Mashl, and J. L. Skinner, "Vibrational energy relaxation in liquids: A mode-coupling approach," *Journal of Physics: Condensed Matter*, vol. 5, no. 16, pp. 2533–2544, 1993.
- [67] F. Könz, Y. Sun, C. W. Thiel, R. L. Cone, R. W. Equall, R. L. Hutcheson, and R. M. Macfarlane, "Temperature and concentration dependence of optical dephasing, spectral-hole lifetime and anisotropic absorption in $\text{Eu}^{3+} : \text{Y}_2\text{SiO}_5$," *Physical Review B*, vol. 68, p. 085109, 2003.
- [68] A. M. Stoneham, "Shapes of Inhomogeneously Broadened Resonance Lines in Solids," *Rev. Mod. Phys.*, vol. 41, pp. 82–108, Jan 1969.
- [69] N. I. Agladze, M. N. Popova, M. A. Koreiba, B. Z. Malkin, and V. R. Pekurovskii, "Isotope Effects in the Lattice Structure and Vibrational and Optical Spectra of $\text{LiYF}_4:\text{Ho}$ Crystals," *Zh. Eksp. Teor. Fiz.*, vol. 104, pp. 4171–4193, 1993. In Russian.
- [70] E. P. Chukalina, M. N. Popova, S. L. Korableva, and R. Y. Abdulsabirov, "Fine structure of spectral lines in $\text{LiYF}_4:\text{Er}^{3+}$ due to isotopic disorder in the lattice," *Physics Letters A*, vol. 269, no. 5–6, pp. 348–352, 2000.
- [71] A. Ferrier, C. W. Thiel, B. Tumino, M. O. Ramirez, L. E. Bausá, R. L. Cone, A. Ikesue, and P. Goldner, "Narrow inhomogeneous and homogeneous optical linewidths in a rare earth doped transparent ceramic," *Physical Review B*, vol. 87, no. 4, p. 041102, 2013.
- [72] K. Karlsson, N. Kunkel, A. Ikesue, A. Ferrier, and P. Goldner, "Nuclear spin coherence properties of $^{151}\text{Eu}^{3+}$ and $^{153}\text{Eu}^{3+}$ in a Y_2O_3 transparent ceramic," *Journal of*

Physics: Condensed Matter, vol. 29, no. 12, p. 125501, 2017.

- [73] W. R. Babbitt, A. Lezama, and T. W. Mossberg, “Optical dephasing, hyperfine structure, and hyperfine relaxation associated with the 580.8-nm $^7F_0 \rightarrow ^5D_0$ transition of europium in $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$,” *Physical Review B*, vol. 39, no. 4, pp. 1987–1992, 1989.
- [74] A. Kinos, *Light-Matter Interaction and Quantum Computing in Rare-Earth-Ion-Doped Crystals*. Doctoral thesis, Lund University, Lund, Sweden, 2018.
- [75] R. J. Gaboriaud, F. Pailloux, P. Guerin, and F. Paumier, “Yttrium oxide thin films, Y_2O_3 , grown by ion beam sputtering on Si,” *Journal of Physics D: Applied Physics*, vol. 33, no. 22, pp. 2884–2889, 2000.
- [76] A. Holzäpfel, J. Etesse, K. T. Kaczmarek, A. Tiranov, N. Gisin, and M. Afzelius, “Optical storage for 0.53 seconds in a solid-state atomic frequency comb memory using dynamical decoupling,” *New Journal of Physics*, vol. 22, no. 6, p. 063009, 2020.
- [77] A. Ortu, A. Holzäpfel, J. Etesse, and M. Afzelius, “Storage of photonic time-bin qubits for up to 20 ms in a rare-earth doped crystal,” *npj Quantum Information*, vol. 8, no. 1, p. 29, 2022.
- [78] A. Ruskuc, C.-J. Wu, E. Green, S. L. N. Hermans, J. Choi, and A. Faraon, “Scalable Multipartite Entanglement of Remote Rare-earth Ion Qubits,” 2024.
- [79] M. Nilsson, L. Rippe, S. Kröll, R. Klieber, and D. Suter, “Hole-burning techniques for isolation and study of individual hyperfine transitions in inhomogeneously broadened solids demonstrated in $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$,” *Physical Review B*, vol. 70, no. 21, p. 214116, 2004.
- [80] J. M. Kindem, A. Ruskuc, J. G. Bartholomew, J. Rochman, Y. Q. Huan, and A. Faraon, “Control and single-shot readout of an ion embedded in a nanophotonic cavity,” *Nature*, vol. 580, pp. 201–204, 2020.
- [81] Karlsruher Institut für Technologie, “Scalable Rare Earth Ion Quantum Computing Nodes (SQUARE).” <https://cordis.europa.eu/project/id/820391/results/de>, 2022. EU Horizon 2020 Forschungsprojekt Nr. 820391, abgeschlossen im März 2022.
- [82] N. Gershenfeld and I. L. Chuang, “Bulk spin-resonance quantum computation,” *Science*, vol. 275, pp. 350–356, 1997.
- [83] D. G. Cory, A. F. Fahmy, and T. F. Havel, “Ensemble quantum computing by NMR spectroscopy,” *Proceedings of the National Academy of Sciences*, vol. 94, no. 5, pp. 1634–1639, 1997.

- [84] S. Chen, M. Raha, C. M. Phenicie, S. Ourari, and J. D. Thompson, “Parallel single-shot measurement and coherent control of solid-state spins below the diffraction limit,” *Science*, vol. 370, no. 6516, pp. 592–595, 2020.
- [85] C. M. Knaut, A. Suleymanzade, Y.-C. Wei, D. R. Assumpcao, P.-J. Stas, Y. Q. Huan, B. Machielse, E. N. Knall, M. Sutula, G. Baranes, N. Sinclair, C. De-Eknamkul, D. S. Levonian, M. K. Bhaskar, H. Park, M. Lončar, and M. D. Lukin, “Entanglement of nanophotonic quantum memory nodes in a telecom network,” *Nature*, vol. 629, pp. 573–578, 2024.
- [86] M. Pompili, S. L. N. Hermans, S. Baier, H. K. C. Beukers, P. C. Humphreys, R. N. Schouten, R. F. L. Vermeulen, M. J. Tiggelman, L. dos Santos Martins, B. Dirkse, S. Wehner, and R. Hanson, “Realization of a multinode quantum network of remote solid-state qubits,” *Science*, vol. 372, no. 6539, pp. 259–264, 2021.
- [87] S. Ourari, Ł. Dusanowski, S. P. Horvath, M. T. Uysal, C. M. Phenicie, P. Stevenson, M. Raha, S. Chen, R. J. Cava, N. P. de Leon, and J. D. Thompson, “Indistinguishable telecom band photons from a single Er ion in the solid state,” *Nature*, vol. 620, pp. 977–981, August 2023.
- [88] I. Usmani, C. Clausen, F. Bussi eres, N. Sangouard, M. Afzelius, and N. Gisin, “Heralded quantum entanglement between two crystals,” *Nature Photonics*, vol. 6, pp. 234–237, 2012.
- [89] D. Hunger, T. Steinmetz, Y. Colombe, C. Deutsch, T. W. H ansch, and J. Reichel, “Fiber Fabry–Perot cavity with high finesse,” *New Journal of Physics*, vol. 12, no. 6, p. 065038, 2010.
- [90] J. Preskill, “Quantum Computing in the NISQ Era and Beyond,” *Quantum*, vol. 2, p. 79, 2018.
- [91] X. Cheng, “Coherent optical spectroscopy of novel rare earth ion materials,” master’s thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2021.
- [92] Sirah Lasertechnik, *Matisse User’s Guide Version 2.5*, 2021.
- [93] A. Franzen, “Componentlibrary.” <https://www.gwoptics.org/ComponentLibrary>, 2025. Licensed under Creative Commons Attribution-NonCommercial 3.0 Unported (<https://creativecommons.org/licenses/by-nc/3.0>).
- [94] Keysight Technologies, “M3300A Datasheet,” tech. rep., Keysight Technologies, 2018. Accessed: 2025-04-21.
- [95] Quantum Machines, *Quantum Orchestration Platform*, 2022. Specification sheet.
- [96] E. A. Donley, T. P. Heavner, F. Levi, M. O. Tataw, and S. R. Jefferts, “Double-pass acousto-optic modulator system,” *Review of Scientific Instruments*, vol. 76,

- no. 063112, 2005.
- [97] D. J. McCarron, “A Guide to Acousto-Optic Modulators,” 2007.
- [98] B. Lauritzen, *Quantum Memories for Telecommunication Networks*. Phd thesis, Université de Genève, 2010.
- [99] C. Laplane, *Generation of non-classical correlations between spins and photons using rare-earth-ion doped crystals*. Phd thesis, Université de Genève, Genève, Switzerland, 2016.
- [100] M. Weber, “Elektronik für Physiker – Vorlesungsskript.” Lecture notes, 2015. Karlsruhe Institute of Technology, Institute for Data Processing and Electronics.
- [101] L. G. Dobbie, “Calculation of Inductance,” in *Radiotron Designer’s Handbook* (F. Langford-Smith, ed.), ch. 10, Sydney, Australia: Wireless Press, 4 ed., 1953.
- [102] Coil32.net, “Coil64 (Coil32) – The freeware coil inductance calculator for radio frequency coils.” <https://coil32.net/theory/self-capacitance.html>, 2015. Accessed: 2025-04-06.
- [103] Quinu. Quinu website: <https://qinu.de/version-lpo>, 2025. Accessed: 2025-04-22.
- [104] A. Zilz, “Investigation of the rarefied gas flow of a $^3\text{He}/^4\text{He}$ dilution refrigerator,” master’s thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2022.
- [105] J. Körber, “Resonator enhancement of tin-vacancy color centers in a single-crystal diamond membrane with a fiber-based scanning cavity,” master’s thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2020.
- [106] D. Schäfter, J. Wischnat, L. Tesi, J. A. D. Sousa, E. Little, J. McGuire, M. Mas-Torrent, C. Rovira, J. Veciana, F. Tuna, N. Crivillers, and J. van Slageren, “Molecular One- and Two-Qubit Systems with Very Long Coherence Times,” *Advanced Materials*, vol. 35, no. 38, p. 2302114, 2023.
- [107] E. Kreidt, C. Kruck, and M. Seitz, “Nonradiative Deactivation of Lanthanoid Luminescence by Multiphonon Relaxation in Molecular Complexes,” in *Handbook on the Physics and Chemistry of Rare Earths*, vol. 53, pp. 35–79, Elsevier, 2018.
- [108] S. Schlittenhardt, E. Vasilenko, V. U. C., N. Jobbitt, O. Fuhr, D. Hunger, M. Ruben, and S. K. Kuppusamy, “Spectral Hole-Burning Studies of a Mononuclear Eu(III) Complex Reveal Narrow Optical Linewidths of the $^5D_0 \rightarrow ^7F_0$ Transition and Seconds-Long Nuclear Spin Lifetimes,” *ChemPhysChem*, vol. 25, no. 19, p. e202400280, 2024.

- [109] T. Krom, “Fluorescence Spectroscopy on Europium using a Confocal Microscope,” bachelor’s thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2018.
- [110] R. Klieber, A. Michalowski, R. Neuhaus, and D. Suter, “Nuclear quadrupole resonance of an electronically excited state from high-resolution hole-burning spectroscopy,” *Physical Review B*, vol. 67, no. 18, p. 184103, 2003.
- [111] R. Oswald, M. G. Hansen, E. Wiens, A. Y. Nevsky, and S. Schiller, “Characteristics of long-lived persistent spectral holes in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ at 1.2 K,” *Physical Review A*, vol. 98, p. 062516, 2018.
- [112] L. E. Erickson, “Optical-RF double resonance measurement of the ground electronic state,” *Optics Communications*, vol. 21, no. 1, pp. 147–149, 1977.
- [113] L. M. K. Vandersypen and I. L. Chuang, “NMR Techniques for Quantum Control and Computation,” *Reviews of Modern Physics*, vol. 76, no. 4, pp. 1037–1069, 2005.
- [114] T. Zhong and P. Goldner, “Emerging rare-earth doped material platforms for quantum nanophotonics,” *Nanophotonics*, vol. 8, no. 11, pp. 2003–2015, 2018.
- [115] R. M. Shelby and R. M. Macfarlane, “Frequency-Dependent Optical Dephasing in the Stoichiometric Material $\text{EuP}_5\text{O}_{14}$,” *Phys. Rev. Lett.*, vol. 45, pp. 1098–1101, Sep 1980.
- [116] E. Vasilenko, V. Unni Chorakkunnath, J. Resch, N. L. Jobbitt, D. Serrano, P. Goldner, S. K. Kuppusamy, M. Ruben, and D. Hunger, “Optically detected nuclear magnetic resonance of coherent spins in a molecular complex,” *Nature Materials*, 2026.
- [117] H. Bauer, J. Blanc, and D. L. Ross, “Octacoordinate Chelates of Lanthanides. Two Series of Compounds,” *Journal of the American Chemical Society*, vol. 86, no. 23, pp. 5125–5131, 1964.
- [118] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, “Synthesis and Fluorescence of Some Trivalent Lanthanide Complexes,” *Journal of the American Chemical Society*, vol. 86, no. 23, pp. 5117–5125, 1964.
- [119] R. P. Sear, “Quantitative studies of crystal nucleation at constant supersaturation: experimental data and models,” *CrystEngComm*, vol. 16, no. 29, pp. 6506–6522, 2014.
- [120] R. Oswald, M. G. Hansen, E. Wiens, A. Y. Nevsky, and S. Schiller, “Characteristics of long-lived persistent spectral holes in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ at 1.2 K,” *Phys. Rev. A*, vol. 98, p. 062516, Dec 2018.
- [121] T. Böttger, C. W. Thiel, Y. Sun, and R. L. Cone, “Optical decoherence and spectral diffusion at 1.5 μm in $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ versus magnetic field, temperature, and Er^{3+} concentration,” *Physical Review B*, vol. 73, p. 075101, 2006.

- [122] M. Lovrić, *Hyperfine Characterisation and Enhanced Optical to Spin Storage in Rare Earth Ion Doped Crystals*. Phd thesis, Technische Universität Dortmund, 2011.
- [123] J. Mlynek, N. C. Wong, R. G. DeVoe, E. S. Kintzer, and R. G. Brewer, “Raman heterodyne detection of nuclear magnetic resonances,” *Physical Review Letters*, vol. 50, pp. 993–996, 1983.
- [124] A. Ulanowski, B. Merkel, and A. Reiserer, “Spectral multiplexing of telecom emitters with stable transition frequency,” *Science Advances*, vol. 8, no. 43, p. eabo4538, 2022.
- [125] I. Karapatzakis, J. Resch, M. Schrodin, P. Fuchs, M. Kieschnick, J. Heupel, L. Kussi, C. Sürgers, C. Popov, J. Meijer, C. Becher, W. Wernsdorfer, and D. Hunger, “Microwave Control of the Tin-Vacancy Spin Qubit in Diamond with a Superconducting Waveguide,” *Physical Review X*, vol. 14, no. 3, p. 031036, 2024.
- [126] Z.-H. Wang, G. de Lange, D. Ristè, R. Hanson, and V. V. Dobrovitski, “Comparison of dynamical decoupling protocols for a nitrogen-vacancy center in diamond,” *Physical Review B*, vol. 85, no. 15, p. 155204, 2012.
- [127] N. Bar-Gill, L. M. Pham, C. Belthangady, D. L. Sage, P. Cappellaro, J. R. Maze, M. D. Lukin, A. Yacoby, and R. Walsworth, “Suppression of spin-bath dynamics for improved coherence of multi-spin-qubit systems,” *Nature Communications*, vol. 3, p. 858, 2012.
- [128] M. Yamaguchi, K. Koyama, and T. Suemoto, “Three-parameter mapping of site distribution by optical-RF double resonance in $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ crystals,” *Journal of Luminescence*, vol. 87–89, pp. 1099–1101, 2000.
- [129] K. S. Pedersen, L. Ungur, M. Sigrist, A. Sundt, M. Schau-Magnussen, V. Vieru, H. Mutka, S. Rols, H. Weihe, O. Waldmann, L. F. Chibotaru, J. Bendix, and J. Dreiser, “Modifying the properties of 4f single-ion magnets by peripheral ligand functionalisation,” *Chemical Science*, vol. 5, no. 4, pp. 1650–1660, 2014.
- [130] Y.-H. Chi, W. Wei, J.-M. Shi, Y.-Q. Zhang, and S.-L. Liu, “Luminescent properties of europium(III) complexes with β -diketonate ligands: Influence of ligand substitution,” *Journal of Coordination Chemistry*, vol. 65, no. 13, pp. 2378–2390, 2012.
- [131] H. J. Batista, A. V. M. Andrade, R. L. Longo, A. M. Simas, G. F. de Sé, N. K. Ito, and L. C. Thompson, “Synthesis, X-ray Structure, Spectroscopic Characterization, and Theoretical Prediction of the Structure and Electronic Spectrum of $[\text{Eu}(\text{btfa})_3 \cdot \text{bipy}]$ and an Assessment of the Effect of Fluorine as a β -Diketone Substituent on the Ligand-Metal Energy Transfer Process,” *Inorganic Chemistry*, vol. 37, no. 14, pp. 3542–3547, 1998.

- [132] E. Vasilenko, V. U. Chorakkunnath, B. Brachnakova, N. L. Jobbitt, S. K. Kuppusamy, D. Hunger, and M. Ruben, "Controlled ion-ion interactions and cavity-enhanced emission of a coherent dinuclear Eu^{3+} complex." submitted, 2026.
- [133] R. Ilmi, W. Sun, J. D. L. Dutra, N. K. Al-Rasbi, L. Zhou, P.-C. Qian, W.-Y. Wong, P. R. Raithby, and M. S. Khan, "Monochromatic red electroluminescence from a homodinuclear europium(III) complex of a β -diketone tethered by 2,2'-bipyrimidine," *Journal of Materials Chemistry C*, vol. 8, pp. 9816–9827, 2020.
- [134] A. Kinos, L. Rippe, S. Kröll, and A. Walther, "Designing gate operations for single-ion quantum computing in rare-earth-ion-doped crystals," *Physical Review A*, vol. 104, no. 5, p. 052624, 2021.
- [135] T. Eichhorn, N. Jobbitt, S. Bieling, S. Liu, T. Krom, D. Serrano, R. Huber, U. Lemmer, H. de Riedmatten, P. Goldner, and D. Hunger, "Multimodal Purcell enhancement and optical coherence of Eu^{3+} ions in a single nanoparticle coupled to a microcavity," *Nanophotonics*, vol. 14, no. 2, pp. 513–522, 2025.
- [136] H.-Y. Wong, W.-S. Lo, W. T. K. Chan, and G.-L. Law, "Mechanistic Investigation of Inducing Triboluminescence in Lanthanide(III) β -Diketonate Complexes," *Inorganic Chemistry*, vol. 56, no. 9, pp. 5135–5140, 2017.
- [137] M. Pallmann, *Purcell-enhanced emission and collective effects of nitrogen-vacancy centers in diamond coupled to a microcavity*. Phd thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2023.
- [138] B. E. A. Saleh and M. C. Teich, *Fundamentals of Photonics*. Hoboken, NJ: Wiley, 2 ed., 2007.
- [139] M. Fox, *Quantum Optics: An Introduction*. Oxford: Oxford University Press, 2013.
- [140] E. Vasilenko, "Development and characterization of a tunable microcavity with integrated diamond membrane for color center spin-photon interfaces," master's thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2019.
- [141] F. Heizmann, "Entwicklung und Charakterisierung einer durchstimmbaren Faser-basierten Mikroresonator Plattform für CQED Anwendungen," bachelor's thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2019.
- [142] J. Körber, M. Pallmann, J. Heupel, R. Stöhr, E. Vasilenko, T. Hümmer, L. Kohler, C. Popov, and D. Hunger, "Scanning Cavity Microscopy of a Single-Crystal Diamond Membrane," *Physical Review Applied*, vol. 19, no. 6, p. 064057, 2023.
- [143] X. Yang, "Cavity-Enhanced Spectroscopy of Rare-earth-ion Based Molecular Complexes," master's thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2024.

- [144] E. Z. Cruzeiro, J. Etesse, A. Tiranov, P.-A. Bourdel, F. Fröwis, P. Goldner, N. Gisin, and M. Afzelius, “Characterization of the hyperfine interaction of the excited 5D_0 state of $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$,” *Physical Review B*, vol. 97, no. 9, p. 094416, 2018.
- [145] J. Schaal, “Fabrication and characterization of superconducting coplanar waveguides for spin qubit control in diamond,” master’s thesis, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2024.

List of Figures

1.1.	Exemplary europium-based molecular complex used throughout this thesis	9
1.2.	Demonstration of coherent nuclear spin control using RF driving	10
2.1.	Representation of the rare-earth elements	14
2.2.	Radial probability density of the $4f$, $5s$, $5p$, and $6s$ orbitals of Eu^{3+}	15
2.3.	Energy level structure of an REI illustrated using the example of Eu^{3+}	16
2.4.	Phonon-induced dephasing mechanisms and lattice distortion in real crystals	28
2.5.	Representation of the inhomogeneous linewidth	34
2.6.	Concept of an REI-based scalable quantum computer	43
3.1.	Optical layout of the Sirah Matisse 2DX Dye laser	49
3.2.	Theoretical PDH error signal of the reference cavity	53
3.3.	Optical setup for ensemble spectroscopy	54
3.4.	Optical setup for measurements of macroscopic samples	57
3.5.	AOM double-pass configuration and control chain	61
3.6.	Exchange gas dipstick cryostat	64
3.7.	Transfer tube and flange dipstick cryostats	66
3.8.	Overview of the RF infrastructure	69
3.9.	Schematic overview of the Qinu LPO cryostat	71
3.10.	Cryogenic confocal setup within the Sionludi cryostat	73
3.11.	Design and modifications of the fiber-based ferrule sample holder	75
3.12.	Asymmetric fiber configuration of the sample holder	78
4.1.	Schematic representation of typical energy transfer mechanisms within a REI-based molecular system	83
4.2.	PL spectrum of an exemplary molecular complex	86
4.3.	Population dynamics and pulse sequence of SHB	88
4.4.	Pump model used for the SHB simulation	90
4.5.	Overview of the nine pump configurations used in the SHB model	91
4.6.	Fitting of the reference SHB data and the corresponding hyperfine splittings of the molecular complex $[\text{Eu}(\text{BA})_4(\text{pip})]$	92
4.7.	Pulse sequence and Bloch vector visualization of the FID	94
4.8.	Pulse sequence and Bloch vector visualization of the photon echo	95
4.9.	Hyperfine lifetime measurement	97
4.10.	Temperature dependence of the spin hole lifetime	98
4.11.	Optically detected nuclear magnetic resonance	100

4.12. Spin echo and dynamical decoupling sequences	101
4.13. Crystal structure of $[\text{Eu}(\text{BA})_4(\text{pip})]$	103
4.14. Macroscopic SKR520 crystals grown by recrystallization	105
4.15. Initial optical characterization of SKR520	108
4.16. SHB measurements of SKR520	109
4.17. Hyperfine lifetime and temperature-dependent optical dephasing of SKR520	110
4.18. Cryo-confocal measurements on a macroscopic SKR520 crystal	111
4.19. Integration of different sample types into the Sionludi cryostat	112
4.20. Comparison of optical properties between powder and macroscopic crystal samples of SKR520 at millikelvin temperatures	113
4.21. Hyperfine lifetime of the macroscopic crystal	114
4.22. FID measurement of SKR520	115
4.23. Photon echo measurements of SKR520	116
4.24. Initial CW ODNMR measurements of the 34 MHz hyperfine transition of SKR520	118
4.25. Preliminary measurements for spin characterization	120
4.26. Spin inhomogeneous line of both hyperfine transitions of SKR520	121
4.27. Power dependence of the 21.5 MHz hyperfine transition of SKR520	121
4.28. Rabi oscillation measurements of the 21.5 MHz hyperfine transition of SKR520	122
4.29. Spin echo measurements of the 21.5 MHz hyperfine transition of SKR520	123
4.30. Spin echo measurements using dynamical decoupling control sequences	124
4.31. Spin hole burning measurements of the 21.5 MHz hyperfine transition of SKR520	126
4.32. Correlation between optical and spin inhomogeneous lines of SKR520	126
4.33. Crystal structure of $[\text{Eu}(\text{trens})]$	127
4.34. Photoluminescence spectra of SKR127	128
4.35. Excited-state lifetime and inhomogeneous linewidth of SKR127	129
4.36. SHB measurements of SKR127	129
4.37. Laser power dependencies of the homogeneous linewidth of SKR127	130
4.38. Temperature-dependent optical dephasing and hyperfine lifetime of SKR127	131
4.39. Molecular structure of $[\text{Eu}(\text{dpphen})(\text{NO}_3)_3]$	133
4.40. Photoluminescence spectra of SKR147	134
4.41. Excited-state lifetime and inhomogeneous linewidth of SKR147	134
4.42. SHB and hyperfine lifetime of SKR147	135
4.43. Molecular structure of $[\text{Eu}(\text{btfa})_3(\text{bipy})]$	136
4.44. Photoluminescence spectra of BB1	137
4.45. Inhomogeneous linewidth and excited-state lifetime of BB1	138
4.46. SHB and hyperfine lifetime of BB1	139
4.47. Characterization of hyperfine splittings of BB1	140
4.48. FID and frequency comb preparation of BB1	141
4.49. Molecular structure of $[\text{Eu}_2(\text{btfa})_6(\text{bpim})]$	142
4.50. Photoluminescence spectra of BB3	143
4.51. Inhomogeneous linewidth and excited-state lifetime of BB3	143
4.52. SHB and hyperfine lifetime of BB3	144
4.53. FID and photon echo of BB3	145

4.54. Comparison of Eu^{3+} -based materials	147
5.1. Exploded and cross-sectional views of the cryo-compatible cavity design	156
5.2. Schematic overview of the optical and control setup of the tube piezo cavity	159
5.3. Visualization of the assembled cavity	161
5.4. Marker grid reference structure used for alignment of the cavity for cooldown	162
5.5. 2D transmission raster scan and finesse measurement	163
5.6. Cavity integration into the cryostats	164
5.7. Measurements during a cooldown in the exchange gas dipstick	165
5.8. Measurement of the passive stability in the Sionludi cryostat	166
5.9. Cavity mirror recrystallization of SKR520 and WLI analysis	169
5.10. Measured mode dispersion of a hybrid cavity containing a molecular micro-crystal	171
5.11. Cavity-mediated fluorescence measurements of SKR520	172
6.1. Outlook: Next steps in ensemble spectroscopy	176
B.1. Resonance characterization of the RF coils	185
C.2. Cross-section of the Sionludi dilution refrigerator	186

List of Tables

2.1.	Summary of selection rules for optical $4f \rightarrow 4f$ transitions	19
2.2.	Comparison of key properties of Y_2SiO_5 (site 1) and Y_2O_3 (C_2) as host materials for Eu^{3+} ions	35
4.1.	Overview of investigated SKR520 samples	107
4.2.	Comparison of key spectroscopic properties of the investigated Eu^{3+} -based molecular complexes throughout this thesis	146
A.1.	Pulse parameters for different optical spectroscopic techniques	182
A.2.	Pulse parameters for different spin spectroscopic techniques	183
B.3.	Parameters used to estimate the magnetic field strength B for both coils . .	184

Erklärung zum Einsatz generativer künstlicher Intelligenz

Die Nutzung generativer künstlicher Intelligenz (KI) im Rahmen dieser Dissertation erfolgte unter Beachtung der Leitlinien des Karlsruher Instituts für Technologie (Stand: 03.06.2025).

In dieser Arbeit wurde generative KI ausschließlich unterstützend zur sprachlichen Überarbeitung von Textabschnitten (insbesondere hinsichtlich Grammatik, Rechtschreibung, Stil und Formulierungen), punktuell zur Literaturrecherche und Identifikation relevanter wissenschaftlicher Publikationen sowie vereinzelt zur technischen Unterstützung bei der Formatierung von LaTeX-Dokumenten und bei programmiertechnischen Fragestellungen eingesetzt.

Generative KI wurde nicht zur Erstellung wissenschaftlicher Inhalte, zur Entwicklung wissenschaftlicher Fragestellungen, zur Analyse oder Interpretation experimenteller Daten sowie zur Ableitung wissenschaftlicher Schlussfolgerungen verwendet.

Die Verantwortung für sämtliche Inhalte, deren wissenschaftliche Richtigkeit sowie die korrekte Zitierung der verwendeten Quellen liegt vollständig beim Autor.

Danksagung

Ich bin ehrlich, es freut mich, endlich mal wieder einen Text in deutscher Sprache zu verfassen. Nach diesem einmonatigen Endspurt seit meiner Rückkehr aus China kann ich mit Freude und ruhigem Gewissen diese Worte hier verfassen, bevor dann die nächste Etappe, meine Verteidigung, bewältigt werden muss. Nichtsdestotrotz möchte ich mich bis dato zuerst bei allen bedanken, die mir vor allem zur Seite standen und mich fachlich sowie moralisch unterstützt haben.

David, dir gebührt natürlich der erste Dank. Ich bin so happy, dass du mich damals nach der Masterarbeit gefragt hast, eine Promotion bei dir zu beginnen. Jeder in unseren Laboren weiß, dass die experimentelle Quantenoptik, sei es Cavity-, Konfokal- oder Ensemblespektroskopie, verdammt nervenaufreibend ist und die gewünschten Erfolge gefühlt nur deltapeak-artig kommen. Trotzdem war es für mich persönlich eine sehr gute Zeit, in der ich viel Erfahrung sammeln konnte. Die Arbeit in einer Forschungsgruppe vergleiche ich sehr gerne mit meinem Lieblingssport Fußball: wir können nur als Team gewinnen und weiterkommen, bezogen auf experimentelle Ergebnisse. Und du, als unser Coach, hast uns wirklich immer zu den richtigen Zeitpunkten den nötigen Input und die Motivation gegeben, weiterzumachen, um erfolgreiche Ergebnisse zu erzielen. Diese Einstellung schätze ich sehr an dir, vor allem den Enthusiasmus und die Freude, die du dabei ausstrahlst. Mein absolutes Highlight war die Messung der schmalen optischen inhomogenen Linie von SKR520, als du dann aus dem Diamantmeeting zu uns ins Wernsdorfer-Labor gesprintet bist und vor Begeisterung für uns eine Vorlesung gehalten hast, welche weiterführenden Schritte wir ausprobieren könnten. Und natürlich, wie deine Frau uns bei deiner Geburtstagskuchenrunde erzählt hat, dass du am Tag der Messung beim Abendessen darüber mit größter Freude berichtet hast. Genau diese sympathische und positive Art schätze ich, bzw. hier kann ich auch im Namen der Gruppe sprechen, schätzen wir sehr an dir, was auch dazu beigetragen hat, dass unsere Gruppenatmosphäre so familiär ist. Vielen Dank für deine Betreuung und dein Vertrauen, es war mir eine Ehre!

An dieser Stelle möchte ich natürlich auch meinem Zweitbetreuer Mario Ruben danken, der zusammen mit Senthil Kumar Kuppusamy unsere Gruppe mit Equipment, fachlicher Unterstützung und vor allem mit vielen Molekülen beliefert hat. Ein weiterer Dank gilt Barbora Brachnakova und Sören Schlittenhardt, die als Teil der Molekül-Kooperation immer für Fragen und Probenherstellung zur Verfügung standen.

Eine große und liebevolle Umarmung geht an meine quasi Zweitfamilie, die Hungerharken oder für mich die Hungenossen. Eine wirklich stabile Truppe mit Humor, fachlicher Kompetenz, und wenn es ums Feiern geht, dann kann uns am Institut keiner das Wasser reichen. Angefangen habe ich mit Larissa, Max, Timon und Jannis, von denen die ersten drei die Gruppe bereits verlassen haben, aber ich möchte euch trotzdem namentlich erwähnen. Es hat mir mit euch allen sehr viel Spaß gemacht. Euer Beitrag war für die Gruppendynamik sehr ausschlaggebend, dafür danke ich euch, dass wir immer was zu lachen oder zu diskutieren hatten. Und ja, Timon, ich schulde dir noch dein Buch von Habeck, kann es aber nicht mehr finden. Ich gehe der Sache nach meiner Verteidigung auf den Grund.

Jetzt würde ich mich gerne beim Tee-Duo Nick und Shalom bedanken, dafür muss ich kurz auf Englisch wechseln, wegen Nick natürlich, der seinen Deutschkurs nicht ernst genommen hat, hehe.

Heeeellouuu

Nick, thank you very much for your support in the last few weeks during writing. And thank you for being such a happy person. You definitely changed the group climate for the better, and your contribution to our language is priceless. I don't even remember what it was like before you. I can only say, I did not expect such a crazy Australian mate ;). Nicky Nick, I wish you the best.

Shalom, I know you can speak German, but now I don't want to change the language again. Shalom, also a big thank you to you. I really have to say that you are on the same level of funniness as Nick, but you express it differently, and this kind of humor is really entertaining. Even though I do not drink tea that often, I really enjoyed talking with you about interesting topics, including food or your country, and of course gossip during the obligatory tea time. And I'll never forget your look in that insider moment! Thank you for showing us where to get good fish and how a real birjani should look.

Tschüssi Süßes and thank you both.

The next big thank you and hug goes to the Team Molecule members, Vishnu and Weizhe. I cannot thank you enough, working with you during my PhD was truly one of the highlights of this journey. I'm grateful that you both joined the group and that we were able to accomplish so much together.

Weizhe, I wish you all the best for your own PhD in Erlangen!

Vishnu, one thank you is not enough. Over the past three years, we've worked side by side, and the results we've achieved together have been incredibly motivating. I'm certain you'll take the work on the molecules even further in the years to come. Thank you not only for being such a great lab partner, but also for being someone I could talk to, especially in the final weeks of writing. Vishnu, thank you for everything. I can only emphasize again how brilliant our teamwork was. It was a true honor to work with you.

Wishing you continued success in everything ahead. I cannot await for you to show me the best federal state in India someday.

So, jetzt kann ich wieder auf Deutsch schreiben. Bei der Gruppe, bei der ich mich als Nächstes bedanken möchte, ist das die Spanien-Urlaubsgruppe: Kerim, Ioannis, Jonas und Jeremias, danke euch, dass ihr es mit mir ausgehalten habt und dass es mit euch so einfach war. Urlaub, das können wir. Aber auch die Zeit an der Uni mit euch hat sehr viel Spaß gemacht, ihr habt immer für eine gute Atmosphäre und Ablenkung gesorgt und, wenn nötig, auch den fachlichen Support geliefert. Ich konnte immer zu euch kommen und um Rat oder Hilfe fragen, auf euch ist Verlass. Auch neben der Uni hat es mich gefreut, Zeit mit euch zu verbringen. Vielen Dank dafür, das nächste Bier geht definitiv auf mich.

Auch den übrigen Gruppenmitgliedern, unseren PhD-Newcomern Andras und Svenja sowie unseren Studierenden Antara, Abhay, Mohammed und Michel, möchte ich für die angenehme Arbeitsatmosphäre und die Hilfsbereitschaft danken. Ein herzliches Dankeschön an die gesamte AG Hunger für das kollegiale Miteinander, die inspirierende Umgebung und viele gemeinsame Kaffee- und Biermomente. Ich hoffe, dieser Spirit bleibt weiterhin erhalten.

Zuletzt möchte ich noch ein paar Worte an meinen besten Freund und meine Familie richten, ohne eure Unterstützung wäre da nicht viel gegangen. Ein großer Dank geht an meinen besten Freund Julka, er hat wirklich jedes Detail meiner Leidens- oder Erfolgsgeschichte mitbekommen und ich bin sehr dankbar, dass du mich hast reden lassen, auch wenn das meiste langweilig oder zum hundertsten Mal wiederholt wurde. Danke dir, Bratan.

Meiner Schwester Nicole möchte ich an dieser Stelle ebenfalls danken, vor allem für zahlreiche Gespräche, moralischen Support und wertvolle Ablenkungen wie Beer Pong, der zu unserem gemeinsamen Lieblingshobby geworden ist. Ich weiß, ich habe dir die Ohren vollgeheult und Panik geschoben und deswegen danke ich dir, dass du mich immer mit den richtigen Worten beruhigen konntest.

Mein letzter Dank gebührt meinen Eltern:

Мама и папа, я вас очень люблю и от всей души благодарю вас за всё, что вы для меня сделали. Я бы хотел выразить свою благодарность, но слов, которыми я хотел бы это сказать, ещё не придумали. Без вас всё это было бы невозможно. Вам — моя огромная благодарность.

Hiermit beende ich dieses Kapitel.

Euer Büro-Gensek,

Evgenij