

Theory of single-molecule NMR detected by real-time ESR

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In relation to recent experimental data [Y. Manassen *et al.*, *J. Magn. Reson.* **374**, 107863 (2025)], we develop a theory framework for demonstrating the feasibility of detecting sharp Nuclear Magnetic Resonance (NMR) oscillations in a real-time ESR data. The procedure is to follow real-time oscillations of the ESR signal measured at a selected frequency of a hyperfine transition. We study a variety of systems such as a single radical molecule with one or two hyperfine coupled nuclei or two molecules that coexist as either radicals or nonradicals, facilitated by charge transfer. We develop a master equation for describing these scenarios and find parameters for which a sharp NMR line can be observed. We show that in all cases an off-diagonal term in the hyperfine tensor is essential for the observation.

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I. INTRODUCTION

The detection of Nuclear Magnetic Resonance (NMR) of individual molecules is an outstanding challenge. This would enable methods in chemical analysis, quantum information, and medical NMR. A variety of methods were attempted: the recent real-time ESR method [1], magnetic resonance force microscopy [2,3], using NV centers [4–6], optically detected magnetic resonance [7,8], rf spin pumping [9], transport methods [10,11], or STM-ENDOR methods [12,13]. Recently a technique was developed for a real-time analysis of electron-spin-resonance by scanning-tunneling-microscope (ESR-STM) signals, that via a hyperfine coupling can detect NMR oscillations [1].

In this paper we develop a theory for NMR detection via real-time ESR in a single molecule. The input data is single-molecule ESR intensity as function of time, at a chosen frequency in the vicinity of a hyperfine line. The ESR data can be detected by either an STM current noise [1] or by other methods [14–16]. Our theory is independent of how the ESR is measured, however, it is essential that this input data is measured during time steps that are shorter than the nuclear precession period as well as longer than the electron precession time, as achieved in Ref. [1]; this scheme is effectively a nonequilibrium detection. These conditions are needed so that the ESR is well defined (i.e., many ESR precessions) and yet the nuclear spin is at an instantaneous value within its precession. In the following, whenever we mention NMR we mean this particular single-molecule NMR detected by real-time ESR.

Our real-time method is therefore distinct from all previous methods for single-molecule NMR [2–13]. Furthermore, we note that our method yields the NMR spectra of nuclei in a single molecule to an accuracy of a few Hz with a linewidth

of ~ 10 Hz [1], allowing, e.g., for detection of chemical shifts. Combining the STM scanning capability and its spatial resolution of ≈ 1 nm show that this method is superior to the previous methods [2–13].

We find a few scenarios depending on parameters that result in sharp NMR lines. In all cases an off-diagonal hyperfine element is essential, as possible in a rotated molecule relative to the magnetic field axis (see Appendix A). We first consider a single radical molecule that has a nucleus with a weak hyperfine coupling relative to the ESR linewidth. The resulting sharp NMR line is a manifestation of motional narrowing. A variant of this case is a radical with two nuclei, one that has weak hyperfine coupling showing sharp NMR, while the second nucleus has strong hyperfine coupling, allowing for hyperfine splitting of the ESR line.

An extension of this model allows the presence of a second molecule allowing charge transfer between the molecules (ionization), so that both molecules coexist as either radicals or nonradicals. A second radical is actually essential for observing ESR-STM [17]. We consider strong intermolecular dissipative transitions while the intramolecular electron spin relaxation is weak in one molecule and strong in the other one. Within our master equation we find scenarios, in which a sharp NMR resonance is possible while the ESR spectrum is broadened and hyperfine splitting is not seen. We have extended the model to a nonequilibrium situation, where the rates of forward and backward ionization transitions are distinct and alternate in time. This alternation is caused by the voltage modulation as in the experimental data [1]. Unlike the equilibrium case we find that one can observe NMR and simultaneously hyperfine split ESR. To determine which scenario corresponds to the actual data a detailed ESR study is needed. A brief summary of all cases is provided in Table I in the conclusions.

II. SINGLE-MOLECULE CASE

A. NMR with one nuclear spin

We consider a single electron spin coupled to a single nuclear spin. The Hamiltonian reads

$$\begin{aligned}\mathcal{H} &= \frac{1}{2}\nu_e\sigma_z + \frac{1}{2}\nu_n\tau_z + \sigma_z(a\tau_z + d\tau_y) \\ &= \frac{1}{2}\nu_e\sigma_z + \frac{1}{2}\nu_n\tau_z + \tilde{a}\sigma_z\tilde{\tau},\end{aligned}\quad (1)$$

where ν_e , ν_n are the electron and nuclear free precession frequencies, respectively, and σ , τ are Pauli matrices for the electron and nuclear spins, respectively. A rotated molecule has in general an off-diagonal term, i.e., $d \neq 0$, see Appendix A. We neglect other hyperfine elements, e.g., $\sim\sigma_x\tau_x$, as these lead to second-order shifts.

We have introduced

$$\tilde{\tau} \equiv \frac{1}{\tilde{a}}(a\tau_z + d\tau_y), \quad \tilde{a} = \sqrt{a^2 + d^2}. \quad (2)$$

We assume that only the electronic spin is subject to relaxation (either due to the coupling to the thermal bath or due to the continuous ESR measurement). This process is characterized by two rates: Γ_d - the rate of spin flips $\uparrow \rightarrow \downarrow$ and Γ_u - the rate of spin flips $\downarrow \rightarrow \uparrow$.

The simplest scenario is when the electronic spin polarization σ_z fluctuates on a time scale much faster than ν_n and averages almost to zero. This scenario, akin to the motional narrowing, allows for a sharp NMR resonance. It requires $\Gamma_1 \gg \tilde{a}$, where $\Gamma_1 \equiv \Gamma_u + \Gamma_d$ is the longitudinal relaxation rate of the electronic spin (related to the ESR linewidth). More specifically, the time evolution of the nuclear raising operator $\tilde{\tau}_+$ (that describes the nuclear spin precession), neglecting here ν_n , is given by

$$\tilde{\tau}_+(t) = e^{-i\tilde{a}\tilde{\tau} \int_0^t \sigma_z(t')dt'} \tilde{\tau}_+ e^{i\tilde{a}\tilde{\tau} \int_0^t \sigma_z(t')dt'} = e^{-2i\tilde{a} \int_0^t \sigma_z(t')dt'} \tilde{\tau}_+. \quad (3)$$

To average over the fast dynamics of $\sigma_z(t)$ we use

$$\langle \delta\sigma_z(t)\delta\sigma_z \rangle_\omega = (1 - \langle \sigma_z \rangle^2) \frac{2\Gamma_1}{\omega^2 + \Gamma_1^2}, \quad (4)$$

where $\delta\sigma_z \equiv \sigma_z - \langle \sigma_z \rangle$ and $\langle \sigma_z \rangle = (\Gamma_u - \Gamma_d)/\Gamma_1$. As a result one obtains

$$\langle \tilde{\tau}_+(t) \rangle \sim \langle e^{-2i\tilde{a} \int_0^t \sigma_z(t')dt'} \rangle = e^{-2i\tilde{a}\langle \sigma_z \rangle t} e^{-\frac{4\tilde{a}^2}{\Gamma_1}(1 - \langle \sigma_z \rangle^2)t}. \quad (5)$$

The first (oscillating) exponent corresponds to a chemical shift of the nuclear Larmor frequency, whereas the second (decaying) exponent gives the nuclear linewidth. If ν_n is taken into account, the coupling to the nuclear spin is not purely longitudinal, i.e., $d \neq 0$ and $\tilde{\tau} \neq \tau_z$, and the dephasing rate of the nuclear spin is small, i.e., $4(1 - \langle \sigma_z \rangle^2)\tilde{a}^2/\Gamma_1 \ll \nu_n$ (motional narrowing), we expect $\tilde{\tau}$ to perform slowly decaying oscillations with frequency close to ν_n , as needed for observing NMR. This derivation is extended in Appendix B to the case of small Γ_1 .

We write down the Lindblad equation governing the dynamics of the system's density matrix

$$\begin{aligned}\frac{d\rho}{dt} &= L\rho = -i[\mathcal{H}, \rho] \\ &+ \Gamma_d \left[\sigma_- \rho \sigma_+ - \frac{1}{2}\sigma_+ \sigma_- \rho - \frac{1}{2}\rho \sigma_+ \sigma_- \right] \\ &+ \Gamma_u \left[\sigma_+ \rho \sigma_- - \frac{1}{2}\sigma_- \sigma_+ \rho - \frac{1}{2}\rho \sigma_- \sigma_+ \right].\end{aligned}\quad (6)$$

In general there is also a pure dephasing rate Γ_ϕ that represents fluctuations coupled to σ_z and then the ESR linewidth is $\Gamma_2 = \frac{1}{2}\Gamma_1 + \Gamma_\phi$. It was shown that Γ_1 and Γ_ϕ are comparable in the STM scenario with high voltage [17,18]. We neglect here Γ_ϕ to emphasize the spin relaxation effect, otherwise Γ_ϕ would effectively enhance Γ_2 . The Lindbladian Eq. (6) allows investigating the ESR response function $C^{-+}(\omega)$:

$$C^{-+}(\omega) = \int_0^\infty \langle \sigma_-(t)\sigma_+(0) \rangle e^{i\omega t} dt. \quad (7)$$

We will be interested (for $\omega > 0$) in

$$C(\omega) = \int_{-\infty}^\infty \langle \sigma_-(t)\sigma_+(0) \rangle e^{i\omega t} dt = 2\text{Re}[C^{-+}(\omega)]. \quad (8)$$

It is easy to obtain $C(\omega)$ in the limit $\nu_n = 0$, i.e., when $\tilde{\tau}$ is a constant of motion. We obtain

$$C^{-+}(\omega) = \frac{1 - \langle \sigma_z \rangle}{2} \frac{1}{i(\nu_e + 2\tilde{a}\tilde{\tau} - \omega) + \Gamma_2}, \quad (9)$$

which gives

$$C(\omega) = \frac{1 - \langle \sigma_z \rangle}{2} \frac{2\Gamma_2}{(\omega - \nu_e - 2\tilde{a}\tilde{\tau})^2 + \Gamma_2^2}. \quad (10)$$

We can expand, assuming $2\tilde{a} \ll \Gamma_2$,

$$C(\omega) \approx \frac{1 - \langle \sigma_z \rangle}{2} \left[\frac{2\Gamma_2}{(\omega - \nu_e)^2 + \Gamma_2^2} + \frac{4\Gamma_2\tilde{a}\tilde{\tau}(\omega - \nu_e)}{((\omega - \nu_e)^2 + \Gamma_2^2)^2} \right]. \quad (11)$$

The correction proportional to $\tilde{\tau}$ is essentially the overlap of $\tilde{\tau}$ and $C(\omega)$. It is maximal around $|\omega - \nu_e| \approx \Gamma_1$. Thus, at its maximum, the correction is of relative order $\tilde{a}/\Gamma_1$. This overlap is quantified in the following numerical study. Since for sharp NMR we need $\tilde{a}/\Gamma_1 \ll \nu_n/\tilde{a}$, we infer that the ratio of the overlap to ESR signal is bounded by $\nu_n/\tilde{a}$.

In the opposite limit $2\tilde{a} \gg \Gamma_1$ we obtain two resolved peaks at $\omega = \nu_e \pm 2\tilde{a}$, corresponding to $\tilde{\tau} = \pm 1$. The overlap is then large.

For $\nu_n \neq 0$ we resort to numerics. We introduce first superoperators so that objects like $A\rho B$ are written as

$$(A\rho B)_{ij} = A_{in}\rho_{nm}B_{mj} = A_{in}(B^T)_{jm}\rho_{nm} = (A \otimes B^T)_{ij,nm}\rho_{nm}. \quad (12)$$

This way ρ_{nm} becomes vectorized with nm being a composite index. Note, that Tr , e.g., in (13) is still the usual trace, namely $\text{Tr}(A\rho B) = (A\rho B)_{ii} = (A \otimes B^T)_{ii,nm}\rho_{nm}$. We then employ the quantum regression theorem, which gives

$$\langle \sigma_-(t)\sigma_+(0) \rangle = \text{Tr}[(\sigma_- \otimes I_d) e^{Lt} (\sigma_+ \otimes I_d) \rho_\infty]. \quad (13)$$

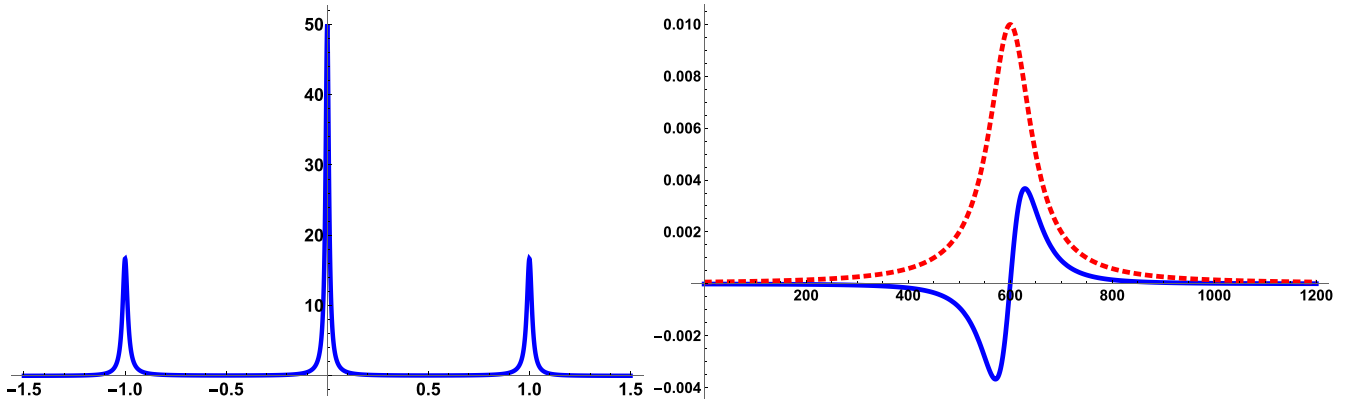


FIG. 1. Left panel: NMR Spectrum, $C_{nmr}(\nu)$. Right panel: The overlap function $\langle \hat{C}(\omega)\bar{\tau} \rangle$ (blue, enhanced by factor 20 for clarity) and the ESR spectrum $C(\omega)$ (red, dashed) as functions of ω . Parameters are $\nu_e = 600$, $\nu_n = 1$, $a = 0.5$, $d = 0.5$, $\Gamma_u = \Gamma_d = 50$. We observe a weak overlap of order of $\tilde{a}/\Gamma_1$.

Here ρ_∞ is the stationary solution of the Lindblad equation $L\rho_\infty = 0$, where L is the superoperator representation of Eq. (6) and $\sigma_\pm$ is transformed to superoperators $\sigma_\pm \otimes I_d$ as well, I_d is a unit matrix of dimension $d = 4$ in this case.

Performing the Fourier (Laplace) transform we get

$$C^{++}(\omega) = \text{Tr} \left[(\sigma_- \otimes I_d) \frac{1}{-i\omega - L} (\sigma_+ \otimes I_d) \rho_\infty \right]. \quad (14)$$

To proceed with our goal of simulating the NMR-STM experiment, consider first a qualitative argument. Assume the hyperfine splitting is well resolved, i.e., the ESR spectrum consists of two narrow peaks at $\omega_\pm = \nu_e \pm 2\tilde{a}$. This regime is achieved if $\Gamma_d, \Gamma_u \ll \tilde{a}$. The peak at ω_+ is observed if the nuclear spin is in the state such that $\bar{\tau} = 1$, whereas the peak at ω_- is observed if $\bar{\tau} = -1$. If the expectation value of $\bar{\tau}$ would oscillate slowly with frequency close to ν_n the relative weight of the ESR peaks would oscillate accordingly and this could be observed if one measures $C(\omega)$ many times near a certain value of ω (with some bandwidth) and the results are Fourier transformed in order to obtain the power spectrum of the NMR signal.

Unfortunately, in the considered system with one nuclear spin the scenario indicated above is impossible. Indeed, if the hyperfine peaks are resolved, i.e., $\Gamma_d, \Gamma_u \ll \tilde{a}$, and $\Gamma_d, \Gamma_u \gg \nu_n$, the nuclear spin dynamics is suppressed. In the extreme case $\Gamma_d, \Gamma_u \ll \nu_n \ll \tilde{a}$ the NMR peaks reappear at shifted positions (see below).

Interestingly, one can observe the NMR spectrum in the ESR signal in the opposite regime, $\Gamma_d, \Gamma_u \gg \tilde{a}$, i.e., when the hyperfine spectrum is not resolved. More precisely this happens if $\frac{\tilde{a}^2}{\Gamma_u + \Gamma_d} \ll \nu_n$, as in Eq. (5). In this regime the effective hyperfine field experienced by the nuclear spin $\tilde{a}\langle\sigma_z\rangle$ shows fast fluctuations and averages out. The situation is well known under the name “motional narrowing”.

We now turn to the main subject of this work, namely the possibility of the ESR signal $C(\omega)$ to show slow NMR related oscillations. We assume that the ESR signal is measured in consecutive time bins $[t_N - \Delta t/2, t_N + \Delta t/2]$. Thus, the measured signal is $C(\omega, \Delta\omega, t_N)$, where $\Delta\omega \sim 1/\Delta t$ is the bandwidth. The measured signal is spectrally analyzed as a function of t_N at frequency $\nu \ll \Delta\omega$. Effectively, what is

measured is the Fourier transform $S(\nu)$ of the following correlation function $S(t_{N_1} - t_{N_2}) = \langle C(\omega, \Delta\omega, t_{N_1}) C(\omega, \Delta\omega, t_{N_2}) \rangle$.

To estimate the NMR contribution to $S(\nu)$ we introduce the following superoperator that represents the ESR absorption spectrum:

$$\hat{C}(\omega) \equiv (\sigma_- \otimes I_d) \frac{1}{-i\omega - L} (\sigma_+ \otimes I_d) + \text{H.c.} \quad (15)$$

and calculate the overlap between this ESR operator and $\bar{\tau}$,

$$\langle \hat{C}(\omega)\bar{\tau} \rangle = \text{Tr}[\hat{C}(\omega)(\bar{\tau} \otimes I_d)\rho_\infty]. \quad (16)$$

We consider in these expressions $\hat{C}(\omega)$ as implicit function of the times t_N via its dependence on $\bar{\tau}$. We then expand this operator, similar to Eq. (11), as

$$\hat{C}(\omega) = \hat{C}_0(\omega) + \hat{C}_1(\omega)\bar{\tau}(t) \quad (17)$$

so that $\langle \hat{C}_1(\omega) \rangle = \langle \hat{C}(\omega)\bar{\tau} \rangle$ is the overlap. Thus, the observed ESR slow modulation is

$$S(\nu) = \langle \hat{C}_1(\omega) \rangle^2 \langle \bar{\tau}(t)\bar{\tau}(t') \rangle_\nu, \quad (18)$$

with ν the Fourier of $t - t'$ that should detect the NMR frequency. In the numerical solution below we check that $\langle \hat{C}_1(\omega) \rangle < \langle \hat{C}(\omega) \rangle$ to justify the expansion. Thus, the NMR spectrum $C_{nmr}(\nu) = \langle \bar{\tau}(t)\bar{\tau}(t') \rangle_\nu$ is contained in the slow fluctuations of the ESR signal $C(\omega)$, though we should keep in mind that its overall intensity has a possibly small prefactor $\langle \hat{C}(\omega)\bar{\tau} \rangle^2$. The ESR frequency ω can be chosen to maximize the overlap.

The NMR spectrum is calculated using the quantum regression theorem, i.e.,

$$C_{nmr}(\nu) = \text{Re} \left[\text{Tr} \left[(\bar{\tau} \otimes I_d) \frac{1}{-i\nu - L} (\bar{\tau} \otimes I_d) \rho_\infty \right] \right]. \quad (19)$$

The results are shown in Fig. 1 with the nuclear correlation function (19) in the left panel and the overlap (16) in the right panel. We note that the nucleus feels an additional effective magnetic field $\tilde{a}\langle\sigma_z\rangle$ if the electron spin is polarized. However, under an STM bias V the electron spin occupations are determined [17] by eV rather than temperature T , since $eV \gg k_B T$. Hence we assume $\Gamma_u = \Gamma_d$ and the spin polarization $\langle\sigma_z\rangle$ vanishes. The overlap $\langle \hat{C}(\omega)\bar{\tau} \rangle$ can be estimated using Eq. (11),

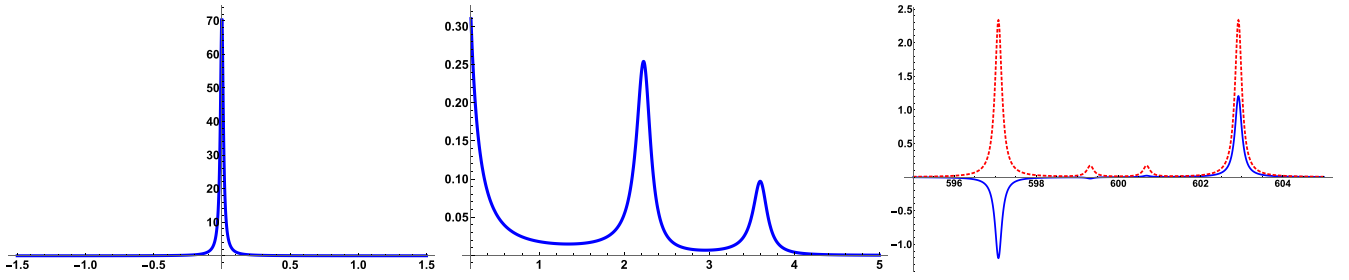


FIG. 2. Left panel: NMR Spectrum, $C_{nmr}(v)$. Middle panel: NMR Spectrum, $C_{nmr}(v)$, at higher frequencies. The peaks correspond to the hyperfine splittings. Right panel: The overlap function $\langle \hat{C}(\omega)\tilde{\tau} \rangle$ (blue, reduced by factor 2 for clarity) and the ESR spectrum $C(\omega)$ (red, dashed) as functions of ω . Parameters are $v_e = 600$, $v_n = 1$, $a = 1.0$, $d = 1.0$, $\Gamma_u = \Gamma_d = 0.1$. The overlap between the ESR signal and $\tilde{\tau}$ is perfect.

indeed we observe that the maximum $\langle \hat{C}(\omega)\tilde{\tau} \rangle \sim \tilde{a}/\Gamma_2$ is achieved at $|\omega - v_e| \sim \Gamma_2$.

For comparison, in Fig. 2, we show the results in the limit of well-resolved ESR hyperfine lines and $\Gamma_d, \Gamma_u \ll v_n$. In this case we see the NMR line at v_n is completely suppressed. Instead, there are weak lines at the shifted positions $\tilde{v}_n \equiv \sqrt{(v_n \pm 2a)^2 + 4d^2}$, corresponding to an effective magnetic field seen by the nucleus at either $\sigma_z = \pm$. Despite the weakness of the spectral lines, the overlap in this case is strong.

B. NMR with two nuclear spins

In almost all molecules there are distinct nuclei with various hyperfine couplings. In particular in toluene there are inequivalent ^1H nuclei with either strong or weak hyperfine coupling [19]. Since the ESR [1] shows fairly strong hyperfine splitting of ~ 10 MHz, while sharp NMR lines result from weakly coupled nuclei we are motivated to study the case of two nuclei spins, one spin with a strong hyperfine coupling, producing the dominant structure in the ESR, while the other with a weak coupling. In particular when the latter hyperfine

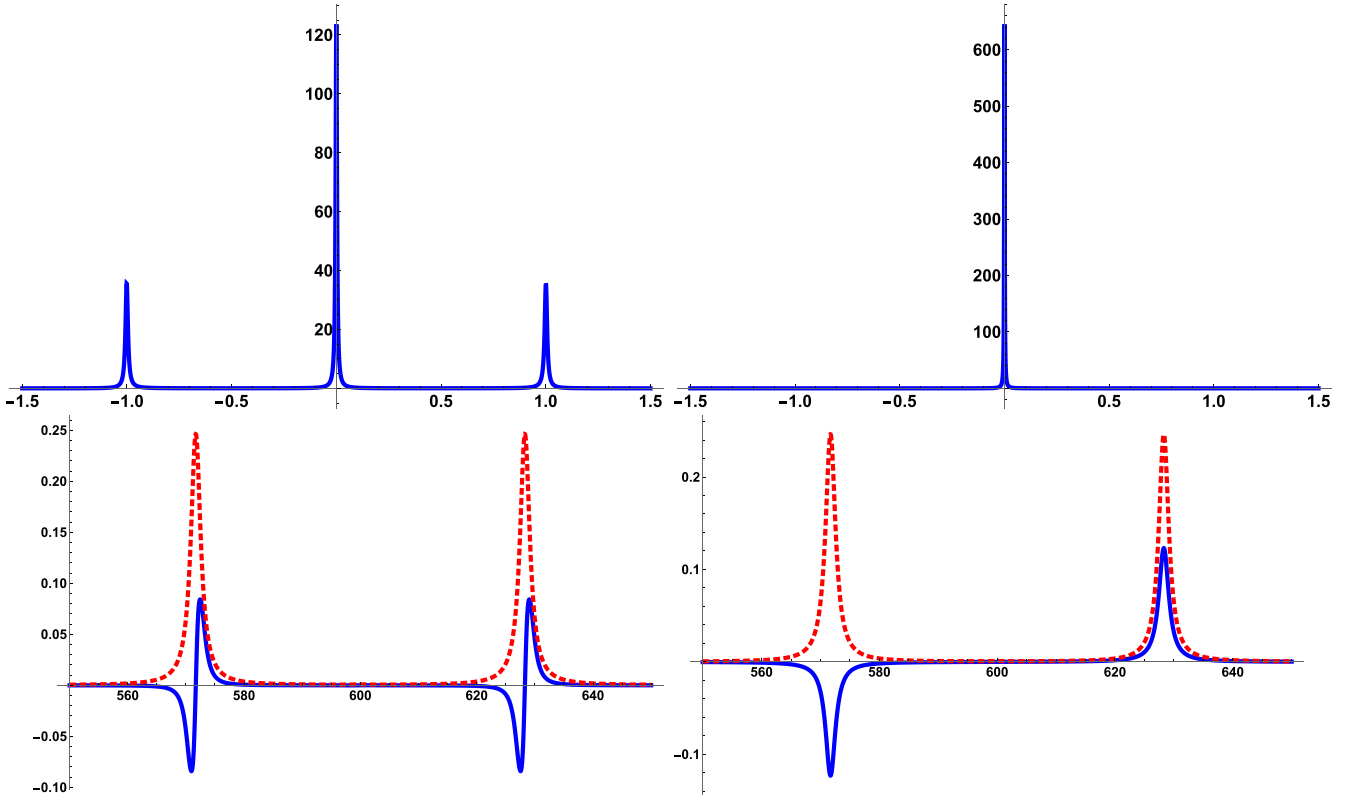


FIG. 3. NMR with two nuclear spins. Left panel, upper part: NMR Spectrum of the weakly coupled spin $\tilde{\tau}_1$. Left panel, lower part: The overlap function $\langle \hat{C}(\omega)\tilde{\tau}_1 \rangle$ (blue, enhanced by factor 5 for clarity) and the ESR spectrum $C(\omega)$ (red, dashed) as functions of ω . Right panel, upper part: NMR Spectrum of the strongly coupled spin $\tilde{\tau}_2$. This spin shows telegraph noise, but no coherent oscillations. Right panel, lower part: The correlation function $\langle \hat{C}(\omega)\tilde{\tau}_2 \rangle$ (blue, suppressed by factor 2 for clarity) and the ESR spectrum $C(\omega)$ (red, dashed) as functions of ω . Parameters are $v_e = 600$, $v_{n,1} = 1$, $v_{n,2} = 1.1$, $a_1 = 0.05$, $d_1 = 0.05$, $a_2 = 10.0$, $d_2 = 10.0$, $\Gamma_u = \Gamma_d = 1.0$.

coupling is weaker than the linewidth then it is not noticeable in the ESR. As we find here, the correlation of the weakly coupled nuclear spin produces a NMR, that is sharper as the ESR linewidth increases.

We consider a single electron spin coupled to two nuclear spins. The Hamiltonian reads

$$\mathcal{H} = \frac{1}{2}\nu_e\sigma_z + \frac{1}{2}\nu_{n,1}\tau_{z,1} + \frac{1}{2}\nu_{n,2}\tau_{z,2} + \sigma_z(\tilde{a}_1\tilde{\tau}_1 + \tilde{a}_2\tilde{\tau}_2), \quad (20)$$

where ($j = 1, 2$)

$$\tilde{\tau}_j \equiv \frac{1}{\tilde{a}_j}(a_j\tau_{z,j} + d_j\tau_{y,j}), \quad \tilde{a}_j = \sqrt{a_j^2 + d_j^2}. \quad (21)$$

The Lindblad equation is identical to (6). We assume the nuclear spin $\tilde{\tau}_2$ to have a strong hyperfine coupling, thus providing the hyperfine-resolved spectrum. The nuclear spin $\tilde{\tau}_1$ is weakly coupled. Therefore, as in the previous section, it is subject to motional narrowing and shows the NMR oscillations as well as the overlap with the ESR signal.

The results are shown in Fig. 3. We again observe correlations between the weakly coupled nuclear spin and the ESR signal. The latter is split by the strongly coupled nuclear spin. We therefore consider this case with two nuclear spins as viable candidates accounting for the data [1].

III. TWO-MOLECULE CASE

We assume here that in addition to the tested molecule that has a nuclear spin the system has an additional spectator molecule that can absorb an ionized electron from the tested one. The advantage of this model is that ionization is included and that nonradical and radical molecules are treated on equal footing. Radical molecules in equilibrium (e.g., TEMPO [1]) become nonradicals upon ionization by an external bias, while nonradical molecules in equilibrium (e.g., toluene [1]) become radicals upon ionization. The case of two radical molecules is labeled as $|11\rangle$, it has two electron spins and one nuclear spin, hence a total of eight states (assuming the nuclear spin is $\frac{1}{2}$). The case of two nonradical molecules is labeled as $|20\rangle$, it has two states, i.e., the whole Hilbert space contains ten states. Evidently, the measured ESR signal comes from the $|11\rangle$ state, however an NMR signal may come from either $|11\rangle$ or from $|20\rangle$. The situation is somewhat similar to

that of two quantum dots [20] that by changing gate voltages can transfer charge between their $|20\rangle$ and $|11\rangle$ states.

The Hamiltonian in the two subspaces, respectively, as well as the total Hamiltonian are

$$\begin{aligned} \mathcal{H}_{11} &= \frac{1}{2}\nu_1\sigma_z + \frac{1}{2}\nu_2s_z + \frac{1}{2}\nu_n\tau_z + a\sigma_z\tau_z + d\sigma_z\tau_y \\ \mathcal{H}_{20} &= \frac{1}{2}\nu_n\tau_z \\ \mathcal{H} &= \mathcal{H}_{11}|11\rangle\langle 11| + \mathcal{H}_{20}|20\rangle\langle 20|, \end{aligned} \quad (22)$$

where σ , s , τ are Pauli matrices representing the two electron spins and the nuclear spin, respectively and ν_1 , ν_2 are the electron resonance frequencies of the two radicals, respectively (in the absence of hyperfine couplings). An additional direct tunneling element between $|11\rangle$ and $|20\rangle$ is possible, as well as a chemical potential shift between these subspaces; we find that both terms have a minor effect on the results in this section.

We assume the switching between the $|11\rangle$ and $|20\rangle$ subspaces to be dissipative. We introduce the rate γ_f for the $|20\rangle \rightarrow |11\rangle$ transition and γ_d for the reverse process. Labeling the states with $\pm$ for σ_z , s_z , and τ_z spins, respectively, we order the $|11\rangle$ space as $|+++, ++-, +-+, +--, -++-, -+-, --+, ---\rangle$. The jump operators couples $|20\rangle$ to just the singlet component of the $|11\rangle$ state, which is either $|0, 0, 0, -1, 0, 1, 0, 0\rangle/\sqrt{2}$ or $|0, 0, -1, 0, 1, 0, 0, 0\rangle/\sqrt{2}$ (i.e., two nuclear spins). We then construct a 10×10 operator jump J that transfers the $|20\rangle$ singlet states into $|11\rangle$, while its transpose J^T is transferring the opposite way. The operator J^T , of dimension 10×10 , has eight rows of zeros while the ninth and tenth rows are

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (23)$$

If $\gamma_f \gg \gamma_b$ the dominant subspace is $|11\rangle$ representing an “ESR” state, while in the opposite case $|20\rangle$ is dominant, it has no ESR.

Since only singlet states are transferred by γ_f , γ_b we consider additional spin relaxations within the $|11\rangle$ states. We define, as in Eq. (6), spin-flip rates for both molecules $\Gamma_d^{(i)}$, $\Gamma_u^{(i)}$, where $i = 1, 2$; in most examples below we consider the regime $\Gamma_d^{(i)} = \Gamma_u^{(i)} \equiv \Gamma^{(i)}$. We define a 10×10 operator $M_1 = \sigma_+ \otimes \mathbb{1} \otimes \mathbb{1}$ and 0 in the 2×2 space of $|20\rangle$, similarly $M_2 = \mathbb{1} \otimes \sigma_+ \otimes \mathbb{1}$. Hence, the Lindblad equation is

$$\begin{aligned} \frac{d\rho}{dt} = L \cdot \rho = & -i[\mathcal{H}, \rho] + \gamma_f \left[J\rho J^\dagger - \frac{1}{2}J^\dagger J\rho - \frac{1}{2}\rho J^\dagger J \right] + \gamma_b \left[J^\dagger \rho J - \frac{1}{2}J J^\dagger \rho - \frac{1}{2}\rho J J^\dagger \right] \\ & + \Gamma_d^{(1)} \left[M_1^\dagger \rho M_1 - \frac{1}{2}M_1^\dagger M_1 \rho - \frac{1}{2}\rho M_1^\dagger M_1 \right] + \Gamma_u^{(1)} \left[M_1 \rho M_1^\dagger - \frac{1}{2}M_1 \rho M_1^\dagger - \frac{1}{2}\rho M_1^\dagger M_1 \right] \\ & + \Gamma_d^{(2)} \left[M_2^\dagger \rho M_2 - \frac{1}{2}M_2^\dagger M_2 \rho - \frac{1}{2}\rho M_2^\dagger M_2 \right] + \Gamma_u^{(2)} \left[M_2 \rho M_2^\dagger - \frac{1}{2}M_2 \rho M_2^\dagger - \frac{1}{2}\rho M_2^\dagger M_2 \right]. \end{aligned} \quad (24)$$

The supermatrices, as in Eq. (12), in a ten-dimensional Hilbert space are now 100×100 . The steady state ρ_∞ is then a 100-dimensional vector that solves $L\rho_\infty = 0$.

We define an NMR operator for the two-molecule case that operates only in the $|11\rangle$ state where ESR is

monitored,

$$\tilde{\tau} = \mathbb{1} \otimes \mathbb{1} \otimes \tilde{\tau} \cdot |11\rangle\langle 11| \oplus 0 \cdot |20\rangle\langle 20| \quad (25)$$

to be used instead of $\tilde{\tau}$ in the single-molecule case. The exclusion of the $|20\rangle$ state reduces the amplitude of the observed

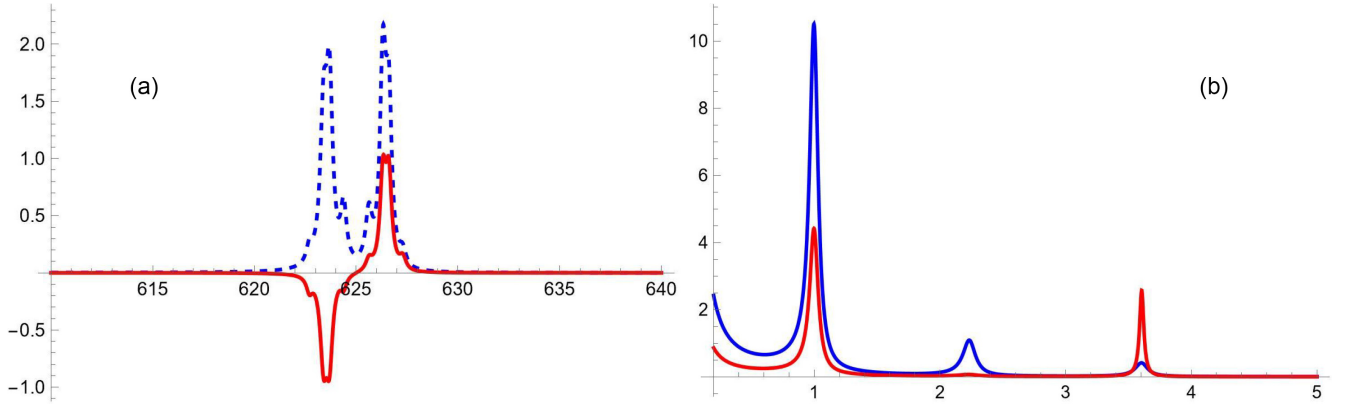


FIG. 4. Two molecules with strong intermolecular $\gamma_f = \gamma_b = 10^4$ and weak intramolecular relaxations. The electron Larmor frequencies are $\nu_1 = 600$, $\nu_2 = 650$ and the hyperfine couplings are $a = d = 1$ while $\Gamma^{(1)} = \Gamma^{(2)} = .03$ [except the red curve in (b)]. (a) ESR spectrum (blue dashed) and its overlap with the nuclear $\tilde{\tau}$ (red). (b) The nuclear correlation with no electron polarization, $\Gamma^{(1)} = \Gamma^{(2)} = .03$ (blue) and with polarization, i.e., $\Gamma_u^{(1)} = \Gamma_u^{(2)} = .05$ and $\Gamma_d^{(1)} = \Gamma_d^{(2)} = .01$ (red).

NMR signal. The exclusion of $|20\rangle$ is essential since in the expansion of $\hat{C}(\omega)$ Eq. (17) only the $|11\rangle$ component affects the measure ESR.

We have found new scenarios for NMR when allowing for large relaxation rates γ_f , γ_b , though still small on the voltage scale (the chemical potential difference of the two molecules is ~ 1 V). We note that in this case the singlet states rapidly decay while the $\Gamma^{(1)}$, $\Gamma^{(2)}$ transitions populate the triplet states, leading to dominance of the latter, hence a strong coupling between the two spins. Projecting the Hamiltonian (keeping only the a , d hyperfine terms) onto the triplet states we find that the ESR frequencies are

$$\nu_{\pm}^{ESR} = \frac{1}{2}[\nu_1 + \nu_2 \pm \nu_n \pm \sqrt{4(a^2 + d^2) - 4a\nu_n + \nu_n^2}]. \quad (26)$$

These frequencies can be detected by measuring ESR of either spin and provide an experimental tool for identifying γ_f , γ_b , i.e., the ESR lines would shift towards these frequencies as γ_f , γ_b increase.

We consider first cases with weak ESR linewidths $\Gamma^{(1)}$, $\Gamma^{(2)}$. The ESR spectrum is shown in Fig. 4(a), showing large overlap/ESR ratio $\sim O(1)$ and sharp NMR frequencies

at $\tilde{\nu}_n = \sqrt{(\nu_n \pm 2a)^2 + (2d)^2}$ as in the single-molecule case (Fig. 2), however we find in this two-molecule case an NMR signal also at the bare ν_n . We note that these frequencies do not shift with an electron polarization since for weak $\Gamma^{(1)}$, $\Gamma^{(2)}$ they correspond to $\sigma_z = \pm 1$, independent of spin polarization. In fact, these cases correspond to extreme chemical shifts, hence they do not depend on shifts in $\langle \sigma_z \rangle \neq \pm 1$. The intensities of these lines, however, do depend on the electron polarization, see Fig. 4(b). We note that this scenario with $\Gamma^{(1)}, \Gamma^{(2)} < \nu_n$ is not realizable in common molecules, unlike the following case.

A second scenario that shows an NMR signal occurs when the coupled molecules are very different. Consider the first molecule with parameters that would show hyperfine split ESR, e.g., $\Gamma^{(1)} = 2$ and $a = d = 2$, however it does not show NMR since the condition $\tilde{a}^2/\Gamma^{(1)} \ll \nu_n$ is not satisfied. The second molecule has a large $\Gamma^{(2)} = 200$, which has no effect if the intermolecular coupling is weak ($\gamma_f = \gamma_b = 0.1$), see blue lines in Fig. 5. However, when the intermolecular coupling becomes large, e.g., $\gamma_f = \gamma_b = 10^4$, the ESR spectrum corresponds to a triplet whose linewidth is dominated by the large $\Gamma^{(2)}$. In this case the ESR does not show hyperfine peaks, however the NMR is seen, see the red lines in Fig. 5. This

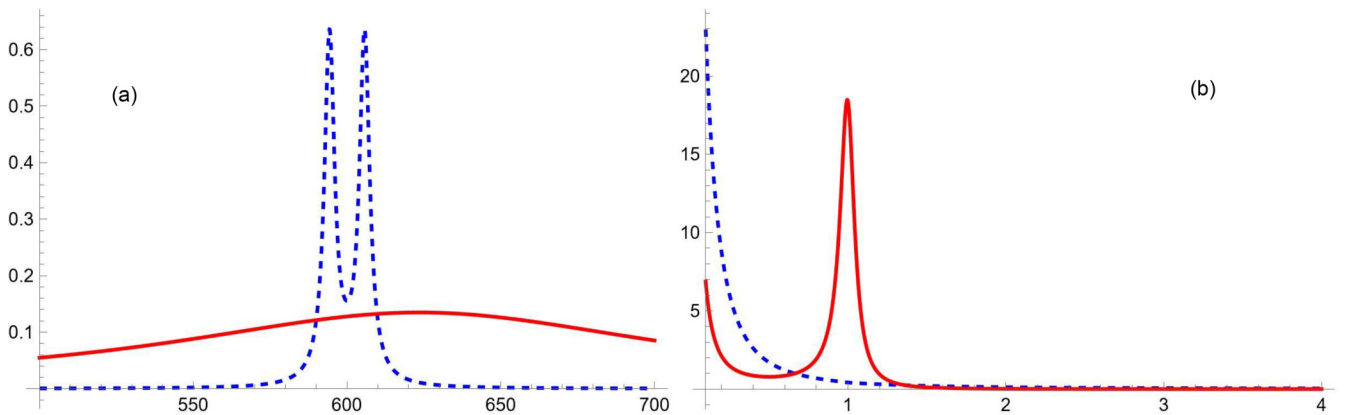


FIG. 5. Effect of intermolecular transition: $\nu_1 = 600$, $\nu_2 = 650$, $\nu_n = 1$, $\Gamma^{(1)} = 2$, $\Gamma^{(2)} = 200$, $a = d = 2$. Compare the cases of strong $\gamma_f = \gamma_b = 10^4$ (red curves) and weak $\gamma_f = \gamma_b = 0.1$ (blue dashed curves) for (a) ESR spectrum and (b) NMR spectrum.

figure shows the trade-off between having a small or large electron relaxation: Weak relaxation shows ESR with hyperfine split lines but no NMR while strong relaxation makes the ESR featureless while an NMR signal is present. This NMR line shifts with the electron polarization, as realized by $\Gamma_u^{(2)} \neq \Gamma_d^{(2)}$ of the stronger relaxation. We infer then that the NMR signal is from the $|11\rangle$ subspace.

The scenario of Fig. 5 can be of practical use. Assume the common situation that we have a molecule with weak $\Gamma^{(1)}$ that shows hyperfine lines, yet it does not show NMR (blue lines). Now imagine that we have at our disposal a second molecule with large electron relaxation $\Gamma^{(2)}$, a molecule that we can move to the vicinity of the first molecule, generating significant couplings γ_f, γ_b . This procedure generates detection of the NMR signal of the first molecule, see red lines in Fig. 5.

The Lindblad operators, exhibited now as superoperators, are then

$$\begin{aligned} LL_1 &= -i\mathcal{H}_1 \otimes I_d + iI_d \otimes \mathcal{H}_1^T + \frac{1}{2}\gamma_f(2J \otimes (J^\dagger)^T - J^\dagger \cdot J \otimes I_d - I_d \otimes [J^\dagger \cdot J]^T) \\ &\quad + \frac{1}{2}\gamma_b(2J^\dagger \otimes J^T - J \cdot J^\dagger \otimes I_d - I_d \otimes [J \cdot J^\dagger]^T) \\ LL_2 &= -i\mathcal{H}_2 \otimes I_d + iI_d \otimes \mathcal{H}_2^T + \frac{1}{2}\gamma_b(2J \otimes (J^\dagger)^T - J^\dagger \cdot J \otimes I_d - I_d \otimes [J^\dagger \cdot J]^T) \\ &\quad + \frac{1}{2}\gamma_f(J^\dagger \otimes J^T - J \cdot J^\dagger \otimes I_d - I_d \otimes [J \cdot J^\dagger]^T) \\ MM_1 &= \frac{1}{2}\Gamma_d^{(1)}[2M_1^\dagger \otimes M_1^T - M_1 \cdot M_1^\dagger \otimes I_d - I_d \otimes (M_1 \cdot M_1^\dagger)^T] \\ &\quad + \frac{1}{2}\Gamma_u^{(1)}[2M_1 \otimes (M_1^\dagger)^T - M_1^\dagger \cdot M_1 \otimes I_d - I_d \otimes (M_1^\dagger \cdot M_1)^T] \end{aligned} \quad (28)$$

and similarly for MM_2 with $1 \rightarrow 2$. The evolution operators for the two time periods are then

$$\begin{aligned} L_1 &= LL_1 + MM_1 + MM_2, \quad \frac{d\rho}{dt} = L_1\rho \Rightarrow \rho(T_1) = e^{L_1 T_1} \rho(0) \\ L_2 &= LL_2 + MM_1 + MM_2, \quad \frac{d\rho}{dt} = L_2\rho \Rightarrow \rho(T_1 + T_2) = e^{L_2 T_2} e^{L_1 T_1} \rho(0). \end{aligned} \quad (29)$$

Hence, the evolution operator for the time $\bar{T}$ is $U = e^{L_2 T_2} e^{L_1 T_1}$. In the simulations below where we use $T_1 = T_2 = .05 \mu$ sec, we find that the results are insensitive to the values of T_1, T_2 as long as they are in the window $1/\nu_1 \ll T_1 + T_2 \ll 1/\nu_n$.

Define eigenvectors $U\rho_i = \lambda_i \rho_i$, hence an expansion $\rho(0) = \sum_{n=1}^{100} c_n \rho_n$ yields after N steps, each of duration $\bar{T} = T_1 + T_2$,

$$\rho(N(\bar{T})) = \sum_n c_n \lambda_n^N \rho_n. \quad (30)$$

We expect that only $n = 1$ has $\lambda_1 = 1$ and $\text{Tr}[\rho_1] = 1$, i.e., ρ_1 is the steady state while for $n > 1$ $|\lambda_n| < 1$ and $\text{Tr}[\rho_n] = 0$ (otherwise the steady state is not unique). The eigenvalues for $n > 1$ $\lambda_n = |\lambda_n| e^{i\varphi_n}$ correspond to eigenfrequencies $\nu_n^* = \varphi_n/\bar{T}$ with linewidth $\Gamma_n = -(\ln |\lambda_n|)/\bar{T}$. One of the ν_n^* will be identified with the nuclear frequency.

For the numerical program (using Mathematica), it is more efficient to find the eigenvectors $v_i^{(1)}$ and eigenvalues $e_i^{(1)}$ of L_1 and then build a matrix E_1 of size 100×100 whose columns are $e_i^{(1)}$. In terms of a diagonal matrix D_1 whose elements are $e_i^{(1) T_1}$ the evolution during T_1 is

$$U_1 = E_1 D_1 (E_1)^{-1} \quad (31)$$

IV. NONEQUILIBRIUM

We consider here the situation [1] where the STM voltage is modulated periodically between a strong and weak value, as often done in the experiment [1]. The Hamiltonian is as defined in (22) and

$$\mathcal{H}_{1,2} = \mathcal{H}_{11}|11\rangle\langle 11| + (\mathcal{H}_{20} \pm V)|20\rangle\langle 20|, \quad (27)$$

where $\mathcal{H}_1$ corresponds to $+V$ and acts during a time T_1 while $\mathcal{H}_2$ corresponds to $-V$ and acts during T_2 . The voltage alternation is then repeated with a total periodicity of $\bar{T} = T_1 + T_2$. We assume that upon voltage change the relaxation rates also switch $\gamma_f \leftrightarrow \gamma_b$, representing stronger relaxation towards the state with the lower voltage. This formalism is fully equivalent to the equilibrium case when $V = 0$ and without $\gamma_f \leftrightarrow \gamma_b$ switching, e.g., when $\gamma_f = \gamma_b$.

and similarly with $1 \rightarrow 2$. Note that the eigenvectors are not orthogonal (L_1 is not Hermitian), we need, however, that E_1 is invertable, otherwise the set of ρ_i cannot span the whole space. The parameter subspace where this condition is violated is known as exceptional points [21] and is of measure zero.

We consider the general case $L_1 \neq L_2$ and evaluate the nuclear correlation using $\bar{\tau}$ of Eq. (25). In the supermatrix notation the density matrices ρ_n in Eq. (22) are vectors (of length 100). Assuming that these vectors span the whole space then $\bar{\tau} \cdot \rho_k = \sum_n d_{kn} \rho_n$. The correlation function, using the regression theorem for $N_1 > N_2$ where N_i correspond to times $N_i \bar{T}$, is

$$\begin{aligned} C_{nmr}(N_1 - N_2) &= \langle \bar{\tau}(N_1) \bar{\tau}(N_2) \rangle = \text{Tr}[\bar{\tau} U^{N_1 - N_2} \bar{\tau} \rho_1] \\ &= \sum_n d_{1n} \lambda_n^{N_1 - N_2} \text{Tr}[\bar{\tau} \rho_n] = \sum_n d_{1n} d_{n1} \lambda_n^{N_1 - N_2} \\ C_{nmr}(v) &= \sum_n d_{1n} d_{n1} \int_0^\infty e^{-\Gamma_n t - i\nu_n^* t + i\nu t} dt + \text{c.c.} \\ &= \sum_n d_{1n} d_{n1} \frac{1}{-i(v - \nu_n^*) + \Gamma_n} + \text{c.c.}, \end{aligned} \quad (32)$$

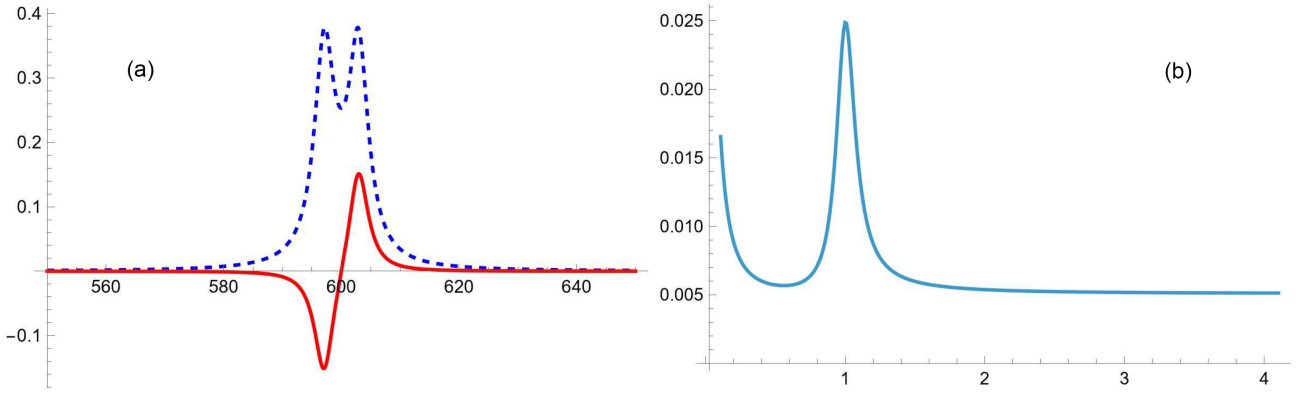


FIG. 6. Nonequilibrium. Consider two molecules with $\gamma_f = 10^4$, $\gamma_b = 0.1$, $V = 0$ and $\nu_1 = 600$, $\nu_2 = 650$, $\nu_n = 1$, $\Gamma^{(1)} = 2$, $\Gamma^{(2)} = 200$, $a = d = 1$. (a) ESR and overlap using equilibrium expressions Eqs. (15) and (16) averaging on the periods T_1 , T_2 . (b) NMR spectra using the nonequilibrium expression (34).

where $\text{Tr}[\rho_n] = \delta_{n,0}$ and the c.c. comes from summation on $N_1 < N_2$. We assume here that the probed frequency is small, i.e., $\nu_n^* \bar{T} \ll 2\pi$ so that the discrete Fourier transform with respect to N can be replaced by integration, i.e., $N \rightarrow t/\bar{T}$. Using a matrix E of eigenvectors $E_{ij} = (\rho_j)_i$ we obtain for the matrix $\hat{d}$, $(\hat{d})_{kn} = d_{kn}$

$$\begin{aligned} (\tilde{\tau} \cdot E)_{ik} &= \sum_j (\tilde{\tau})_{ij} (\rho_k)_j = \sum_n d_{kn} (\rho_n)_i \\ &= \sum_n d_{kn} E_{in} = (E \cdot \hat{d}^T)_{ik} \\ \Rightarrow \hat{d} &= (E^{-1} \cdot \tilde{\tau} \cdot E)^T \end{aligned} \quad (33)$$

which is an efficient way of evaluating d_{kn} . Thus, finally

$$C_{nmr}(\nu) = \sum_{n>0} \text{Re} \left[\frac{2d_{1n}d_{n1}}{-i(\nu - \nu_n^*) + \Gamma_n} \right]. \quad (34)$$

We find numerically that allowing $V \neq 0$ has a minor effect on the previous results. However, allowing $\gamma_f \neq \gamma_b$ leads to a significant effect if $\gamma_f/\gamma_b \gg 1$, as shown in Fig. 6. The case $\gamma_f/\gamma_b \gg 1$ means that the relaxation $|20\rangle \rightarrow |11\rangle$ is dominant so that in the period T_1 the dominant subspace is $|11\rangle$, while $|20\rangle$ is dominant in the period T_2 . The $|11\rangle$ component allows detection of ESR with hyperfine splitting, Fig. 6(a). The ESR is evaluated using the equilibrium formulation Eq. (15) with either $L \rightarrow L_1$ or $L \rightarrow L_2$, since there are many ESR

oscillations in one period T_1 or T_2 ; the actual measurement would average the T_1 and T_2 data (with T_1 dominant), shown in Fig. 6(a). We also evaluate the NMR spectrum, Fig. 6(b), using the nonequilibrium expression Eq. (30), showing a clear signal.

V. CONCLUSIONS

We have found a number of scenarios where real-time analysis of ESR-STM data shows NMR signals. All these scenarios are summarized in Table I for easy access. Note that in all the scenarios we find that an off-diagonal hyperfine coupling $\sim \sigma_z \tau_y$ is essential for NMR observation. In Appendix A we show that a rotated molecule, i.e., the magnetic field is not parallel to a principal axis of the molecule, has in general such an off-diagonal coupling.

We have shown that sharp NMR lines are possible with either $\Gamma_1 \ll \nu_n$ or with $\frac{\tilde{a}^2}{\Gamma_1} \ll \nu_n$, as in the simplified Eq. (5) and in Appendix B. The case with $\Gamma_1 \ll \nu_n$, Figs. 2 and 4 show NMR lines at shifted positions and when two molecules are coupled also at the bare nuclear frequency. This situation of very weak electron relaxation, however, does not apply to known molecules.

We therefore focus on the case $\frac{\tilde{a}^2}{\Gamma_1} \ll \nu_n$, a motional narrowing phenomenon. For a single molecule we consider two nuclei, the dominant one with a strong $\tilde{a}$ that allows observable ESR with hyperfine splitting, while the second nucleus

TABLE I. Parameter regimes for observing sharp NMR lines in terms of the ESR linewidth $\approx \Gamma_1$ (or $\Gamma^{(1)}$, $\Gamma^{(2)}$ for two molecules), hyperfine coupling $\tilde{a}$ defined in Eq. (2) (or $\tilde{a}_1$, $\tilde{a}_2$ for two nuclei), and transition rates γ_f , γ_b for charge transfer between two molecules. All cases have a single nucleus with Larmor frequency ν_n , except when two nuclei are indicated, with comparable ν_n . Also shown is the representative figure number.

Configuration	Parameter regimes	ESR shape	Figure
single molecule	$\frac{\tilde{a}^2}{\Gamma_1} \ll \nu_n$	wide resonance	1
single molecule	$\Gamma_1 \ll \nu_n$, $\tilde{a}$	$\tilde{a}$ splitting	2
single molecule, two nuclei	$\frac{\tilde{a}_1^2}{\Gamma_1} \ll \nu_n$, $\tilde{a}_2 > \Gamma_1$	$\tilde{a}_2$ splitting	3
two molecules	$\Gamma^{(1)}, \Gamma^{(2)} \ll \nu_n$, $\tilde{a}$ $\gamma_f, \gamma_b \gg \tilde{a}$	triplet, $\tilde{a}$ splitting	4
two molecules	$\frac{\tilde{a}^2}{\Gamma^{(2)}} \ll \nu_n$, $\Gamma^{(1)} < \tilde{a}$ $\gamma_f, \gamma_b \gg \tilde{a}$	wide resonance	5
two molecules, γ_f, γ_b alternating	$\frac{\tilde{a}^2}{\Gamma^{(2)}} \ll \nu_n$, $\Gamma^{(1)} < \tilde{a}$ $\gamma_f \gg \tilde{a} > \gamma_b$	$\tilde{a}$ splitting	6

has weak $\tilde{a}$ that allows for a sharp NMR. This scenario applies, e.g., to toluene that has many ^1H nuclei with varying hyperfine couplings.

For cases with a single nucleus in the molecule, e.g., ^{31}P or ^{14}N , we propose scenarios with strongly coupled two molecules such that the spectator molecule has a much larger relaxation rate. Figure 5 shows that NMR appears at strong γ_f , γ_b at the expense of hyperfine structure in ESR. The ESR data on cases with sharp NMR are partial [1], one needs more detailed data on a wider frequency range to determine if this scenario applies. In fact, if one can move a spectator molecule with strong relaxation to the vicinity of a target molecule, then any target nuclear frequency can be detected.

Our final scenario is a nonequilibrium one, i.e., two molecules with different intramolecular relaxation rates, as above, and also $\gamma_f/\gamma_b \gg 1$. As shown in Fig. 6 one can have both ESR with hyperfine structure and a sharp NMR. The relaxation rates are controlled by the STM voltage. The intermolecular relaxation can be deduced from detailed ESR spectra, once available.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: ROTATED HYPERFINE

Suppose that the hyperfine tensor has principal axes z', y', x' at some orientation relative to the magnetic field, chosen in the z direction. The diagonal hyperfine elements are c', b', a' . We wish to rotate this tensor and find the dominant hyperfine splitting for electron Larmor frequency $\nu \gg a', b', c'$. Assume for simplicity that it is sufficient to rotate around the $x = x'$ axis with an angle θ , this is the case if c' is relatively small or if two elements are equal $b' = c'$. The hyperfine coupling with the rotation matrix $R(\theta)$ becomes, where the electron spin is $\mathbf{S}$, the nuclear spin is $\mathbf{I}$, and primes denote rotated quantities,

$$\begin{aligned} \mathbf{S}' \cdot \mathbf{A}' \cdot \mathbf{I}' &= (S_z, S_y, S_x) \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a' & 0 & 0 \\ 0 & b' & 0 \\ 0 & 0 & c' \end{pmatrix} \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} I_z \\ I_y \\ I_x \end{pmatrix} \\ &= (S_z, S_y, S_x) \begin{pmatrix} a' \cos^2 \theta + b' \sin^2 \theta & \sin \theta \cos \theta (b' - a') & 0 \\ \sin \theta \cos \theta (b' - a') & a' \cos^2 \theta + b' \sin^2 \theta & 0 \\ 0 & 0 & c' \end{pmatrix} \begin{pmatrix} I_z \\ I_y \\ I_x \end{pmatrix}, \end{aligned} \quad (\text{A1})$$

where the rotated spin vectors $\mathbf{S} = \mathbf{S}' \cdot R(-\theta)$, $\mathbf{I} = R(\theta) \cdot \mathbf{I}'$. For a general rotation all elements of the tensor become finite. In the presence of a Larmor frequency ν in the Hamiltonian, i.e., νS_z , the S_x , S_y terms are perturbative of order (hyperfine) $^2/\nu$, hence the dominant hyperfine term is

$$\begin{aligned} \mathcal{H}_{\text{hyp}} &= S_z (a I_z + d I_y) = \sqrt{a^2 + d^2} S_z \tilde{I}, \quad \tilde{I} = \frac{a}{\sqrt{a^2 + d^2}} I_z + \frac{d}{\sqrt{a^2 + d^2}} I_y \\ a &= a' \cos^2 \theta + b' \sin^2 \theta, \quad d = \sin \theta \cos \theta (b' - a'), \quad \Rightarrow a^2 + d^2 = a'^2 \cos^2 \theta + b'^2 \sin^2 \theta. \end{aligned} \quad (\text{A2})$$

The eigenvalues $\pm \sqrt{a'^2 \cos^2 \theta + b'^2 \sin^2 \theta}$ are in agreement with Eq. (1.66) (or Eq. (3.44) of Ref. [22]) (the g factor is assumed isotropic). The anisotropic hyperfine tensor with off-diagonal elements is also studied in Secs. 7-6 and 7-7 of Ref. [19], including analysis of experimental data.

APPENDIX B: NUCLEAR DEPHASING FOR $\nu_n = 0$

Consider NMR in a single radical molecule, i.e., one electron and one nuclear spin. Consider the Hamiltonian Eq. (1),

$$\mathcal{H} = \frac{1}{2} \nu \sigma_z + \frac{1}{2} \nu_n \tau_z + \tilde{a} \sigma_z \tilde{\tau}. \quad (\text{B1})$$

In addition there are electron relaxation rates Γ_d , Γ_u . The case of strong relaxations is discussed in Eq. (5). We extend this derivation to a general Γ where $\Gamma \equiv \Gamma_d = \Gamma_u$, and as

in (5) with ν_n neglected. We use the following trick [23]: Define conditional averages $\chi_{\pm}(t) = \langle e^{i2\tilde{a} \int^t \sigma_z(t') dt'} \rangle$, averaged over switching histories ending at $\sigma_z(t) = \pm 1$. These satisfy the rate equations

$$\begin{aligned} \dot{\chi}_+ &= 2i\tilde{a}\chi_+ - \Gamma\chi_+ + \Gamma\chi_-, \\ \dot{\chi}_- &= -2i\tilde{a}\chi_- - \Gamma\chi_- + \Gamma\chi_+, \\ \chi_{1,2} &= \chi_+ \pm \chi_- \Rightarrow \dot{\chi}_1 = 2i\tilde{a}\chi_2, \\ \dot{\chi}_2 &= 2i\tilde{a}\chi_1 - 2\Gamma\chi_2 \\ \Rightarrow \dot{\chi}_2 &= -4\tilde{a}^2\chi_2 - 2\Gamma\dot{\chi}_2 \Rightarrow \omega_{\pm} = i\Gamma \pm \sqrt{4\tilde{a}^2 - \Gamma^2}. \end{aligned} \quad (\text{B2})$$

There are two solutions $\sim e^{i\omega_{\pm}t}$, with the initial conditions $\chi_{\pm}(0) = \frac{1}{2}$ we have

$$\begin{aligned}\chi_2(t) &= \frac{\tilde{a}}{\sqrt{4\tilde{a}^2 - \Gamma^2}} e^{-\Gamma t} [e^{i\sqrt{4\tilde{a}^2 - \Gamma^2}t} - e^{-i\sqrt{4\tilde{a}^2 - \Gamma^2}t}] \\ \chi_1(t) &= e^{-\Gamma t} \left[\cos(\sqrt{4\tilde{a}^2 - \Gamma^2}t) \right. \\ &\quad \left. + \frac{\Gamma}{\sqrt{4\tilde{a}^2 - \Gamma^2}} \sin(\sqrt{4\tilde{a}^2 - \Gamma^2}t) \right].\end{aligned}\quad (\text{B3})$$

Our needed average is $\chi_1(t)$, it defines a dephasing rate via $\chi_1(t) \sim e^{-\gamma_{\varphi}t}$. Hence, for $\Gamma < 2\tilde{a}$ we have $\gamma_{\varphi} = \Gamma$ apart for oscillating terms. For $\Gamma > 2\tilde{a}$ at long times $\chi_1(t) \sim$

$\frac{1}{2}e^{-\Gamma t + \sqrt{\Gamma^2 - 4\tilde{a}^2}t}$, hence the dephasing rate is

$$\begin{aligned}\gamma_{\varphi} &= \Gamma - \sqrt{\Gamma^2 - 4\tilde{a}^2} \quad \Gamma > 2\tilde{a} \\ \gamma_{\varphi} &\rightarrow \frac{2\tilde{a}^2}{\Gamma} \quad \Gamma \gg 2\tilde{a} \\ \gamma_{\varphi} &= \Gamma \quad \Gamma < 2\tilde{a}.\end{aligned}\quad (\text{B4})$$

The $\Gamma \gg 2\tilde{a}$ case agrees with Eq. (5), useful for interpretation of many of our scenarios. One can extend this derivation to the case $\Gamma_d \neq \Gamma_u$ and derive, to leading order in $(\tilde{a}/\Gamma_1)^2$ the result given in (5). The case $\Gamma < 2\tilde{a}$ is less relevant to experimental data, however it is complementary and motivates our small Γ examples in Figs. 2 and 4.

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