ECONOS 2020 2021 Karlsruhe

19th European Conference On Non-Linear Optical Spectroscopy

26 – 29 Sep. 2021, Karlsruhe, Germany

PROCEEDINGS

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19th European Conference On Non-Linear Optical Spectroscopy (ECONOS 2020/2021)

Volume Editors: Ahmed Abdelmonem; Benoît Barviau

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Compared to the printed Book of Abstracts that was handed to the on-site participants at the registration desk, this Book of proceedings contains only the abstracts of work that has been published onsite or online during the conference.

ECONOS
2020
2021
Karlsruhe

PREFACE BY THE CONFERENCE CHAIRMAN

Organizing ECONOS 2020/2021 under the dynamic conditions of the COVID-19 pandemic was a challenge for organizers, participants and sponsors. ECONOS 2020, originally scheduled from April 19th to 22nd 2020, was postponed to May 30th to June 2nd 2021 and then finally to September 26th to 29th 2021 under the name ECONOS 2020/2021. Our intention has always been to mitigate the disappointment and inconvenience for all delegates and sponsors who were looking forward to stimulating scientific discussions during ECONOS 2020. Postponing ECONOS 2020 was not a decision we took lightly. Since the initial COVID outbreak, we have been carefully monitoring the global evolution. In an effort to have health and well-being of all the participants as our top priority, we considered all possible options and contingency plans. The uncertainty in the pandemic evolution and related regulations made the decision a challenge. Our motivation has always been to host the safest and highest quality ECONOS 2020/2021possible, and today, we deliver on that promise.

Abdelmonem

Ahmed Abdelmonem (Conference Chair)

ACKNOWLEDGEMENTS

The conference chairs are grateful to the German Research Foundation for supporting the conference (DFG, AB 604/2-1). We acknowledge the international steering committee for the continuous support during the preparation of the conference. Special thanks to *Prof. Benoît Barviau* (Rouen, France) for his support during finalization of the conference program and the book of abstracts. We also acknowledge the support of the ASERV, RECHT, EVM, FIMA, and FOR departments at KIT. We particularly thank *Mr. Simon Scheuerle* (General Services, KIT) and *Mrs. Kristen Schel-Fu* (Legal Department, KIT) for working closely with the local organization team. The conference chair is particularly grateful to *Prof. Thomas Leisner* (head of IMKAAF-KIT) and *Mrs. Susanne Bolz* (IMKAAF secretary). The 2021 team also thanks former colleague *Mrs. Aya Abdellatif* who exclusively maintained the website and led the communication with invited speakers, participants, sponsors and the conference hotel in a superlative way during the period from July 2019 to September 2020.

ECONOS 2020 2021 Karlsruhe

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Left to right: Clara Saak (U. Vienna), Daria Maltseva (MPIP), Ahmed Abdelmonem, Sylvia Sullivan (IMK-KIT), and Sami Salamin (ITEC-KIT)

- Onsite international steering committee members:

Arnulf Materny, Brigitte Attal-Trétout, and Michele Marrocco

European Conference On Non-Linear Optical Spectroscopy

ECONOS emerged in 2002 to broaden the agenda of the former annual European CARS (Coherent Anti-Stokes Raman Scattering) workshops and cover all forms of nonlinear optical spectroscopy, theoretical and experimental studies, and applications. Topics include, but are not limited to, CARS, and other forms of coherent Raman scattering, applications of high-order responses in the time and frequency domain, development of novel laser sources, as well as developments related to physical processes that give rise to spectral signatures in different media. ECONOS 2020/2021 intends to attract participation from χ^2 NLO spectroscopy, e.g. SFG (Sum-Frequency Generation), as well as to further expand the multidisciplinary nature of ECONOS.

ECONOS in general provides a platform for scientific exchange between physicists, chemists, engineers, material scientists, biologists, biomedical scientists and industry representatives and is intended to provide participants with new momentum and directions for their research. The conference helps to translate multifaceted spectroscopy research into industrial application and marketing, e.g. in the field of new diagnostic and biomedical approaches. ECONOS 2020/2021 has a special aim to attract atmospheric scientists to this community and draw the attention of this community to atmospheric problems.

Selected Papers from the 2020 contributions have been published in a special issue 'ECONOS/ECW 2020' of the Journal of Raman spectroscopy:

Volume 52, Issue 9, Pages: 1491-1666, September 2021
Special Issue: ECONOS/ECW 2020 Special Issue in memoriam of Marcus Motzkus
Issue Edited by: Johannes Kiefer
Link: https://analyticalsciencejournals.onlinelibrary.wiley.com/toc/10974555/2021/52/9

A special issue 'ECONOS/ECW 2021' for 2021 contributions is planned. Author information regarding the preparation of manuscripts can be found on JRS webpage..

HISTORY

Former 18 editions of the ECONOS Meetings:

- ECONOS 2019, Rouen ,France, April 7- 10
- ECONOS 2018, Milan, Italy, April 8-11
- ECONOS 2017, Jena, Germany, April 2-5
- ECONOS 2016, Göteborg, Sweden, April 24-27
- ECONOS 2015, Leuven, Belgium, April 12-15
- ECONOS 2014, Dole, France, May 11-14
- ECONOS 2013, Exeter, UK, April 22-24
- ECONOS 2012, Aberdeen, UK, July 8-11
- ECONOS 2011, Enschede, Netherlands, May 23-25
- ECONOS 2010, Bremen, Germany, Jun 21-23
- ECONOS 2009, Frascati, Italy, May 25-27
- ECONOS 2008, Igls, Austria, May 25-27
- ECONOS 2007, St. Petersburg, Russia, May 12-15
- ECONOS 2006, Smolenice, Slovak Republik, April 9-11
- ECONOS 2005, Oxford, United Kingdom, April 10-12
- ECONOS 2004, Erlangen, Germany, April 4-6
- ECONOS 2003, Besancon, France, March 30,31 and April 1
- ECONOS 2002, Villigen, Switzerland, March 18-19

The conference is named ECONOS since 2002, and was previously called European CARS workshop, starting in 1982:

2001, Lund, Sweden - 2000, Moscow, Russia - 1999, Frascati, Italy - 1998, Besançon, France - 1997, Heidelberg, Germany - 1996, Sheffield, United Kingdom - 1995, Madrid, Spain - 1994, Gif sur Yvette, France - 1993, Villigen, Swiss - 1992, Florence, Italy - 1991, Garching, Germany - 1990, Dijon, France - 1989, Oxford, United Kingdom - 1988, Pisa, Italy - 1987, Stuttgart, Germany - 1986, Lund, Sweden - 1985, Rouen, France - 1984, Harwell, United Kingdom - 1983, Châtillon, France - 1982, Harwell, United Kingdom

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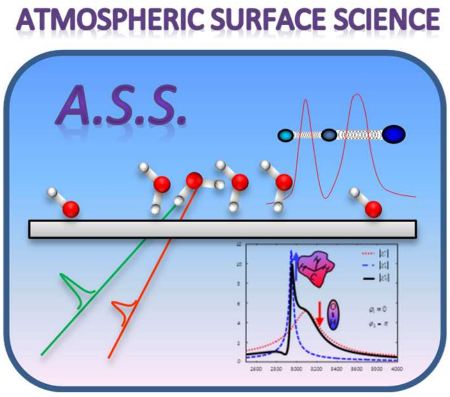

Atmospheric surface-science at Atmospheric Aerosol Research division of the Institute of Meteorology and Climate Research (IMK-AAF), Karlsruhe Institute of Technology.

Funded By:

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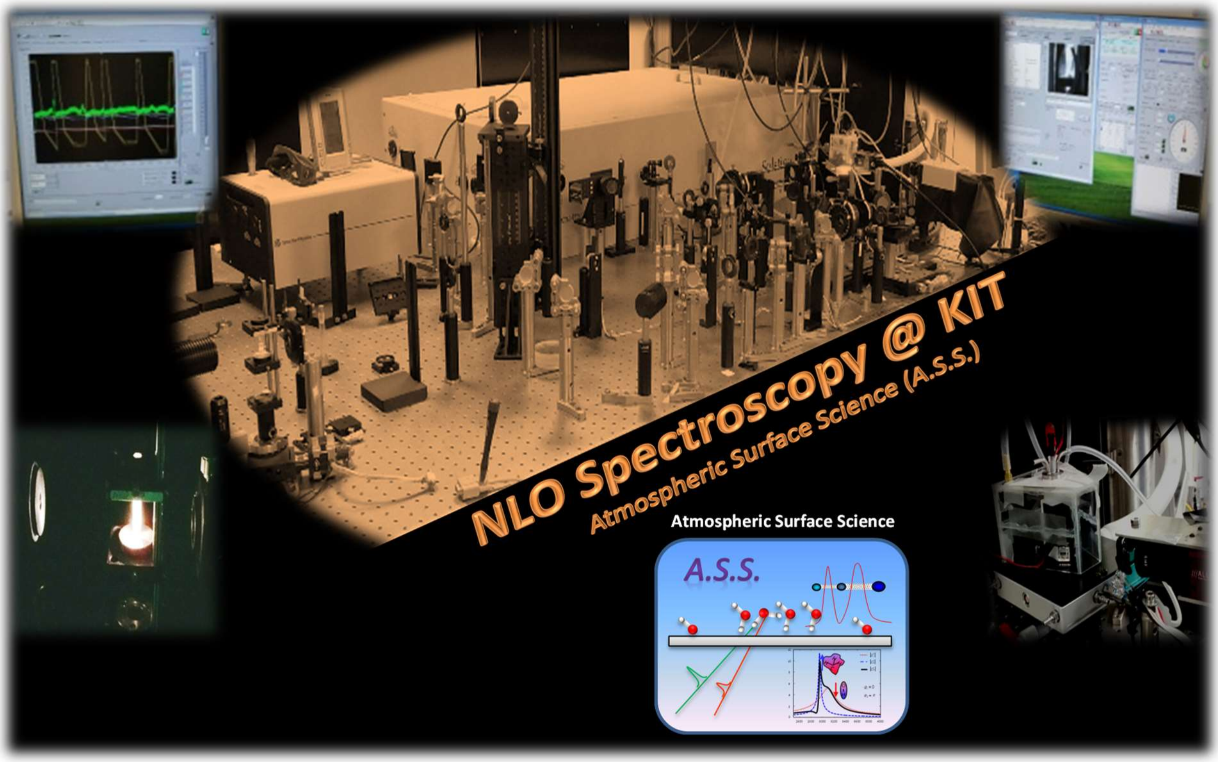
ATMOSPHERIC SURFACE-SCIENCE

Atmospheric Surface-Science (A.S.S.) is a new research line at the KIT, funded by the German Research Foundation (DFG) and has been set out in the Institute of Meteorology and Climate Research – Atmospheric Aerosol Research (IMK-AAF) at KIT after four successful grants:

1. Start-Up-Budget (STUB 2012) in 2012 from the Helmholtz association.
2. Research grant (DFG, AB 604/1-1) in 2014 from the German Research Foundation.
3. Research grant (DFG, AB 604/1-2) in 2017 from the German Research Foundation.
4. Research grant (DFG, AB 604/3-1) in 2020 from the German Research Foundation.

The aim of this research is to investigate atmospheric aerosol-cloud-climate interactions* on the molecular level using NLO spectroscopy.

* Atmospheric interactions of interest include, but are not limited to heterogeneous ice nucleation particle oxidation and photo-sensitization, secondary aerosol and biogenic particle formation, molecular composition-, phase-, acidity- and structure- changes …)



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Ahmed Abdelmonem
Aya Abdellatif

19th European Conference On Non-Linear Optical Spectroscopy (ECONOS 2020/2021)

Conference Program

Date: 26.09. – 29.09. 2021

Sunday September 26th 2021

15:00	Registration		
17:00	**Opening (Conference Chair: Ahmed Abdelmonem, KIT)** Atmospheric Surface-Science research @ KIT (story, goals, achievements)		22
17:40	**Mischa Bonn** Keynote	Novel Molecular Terahertz Spectroscopies	23
18:20	**Welcome**		
20:00	**Day End**		

Monday September 27th 2021

08:00		Registration		
08:40	**High-order responses in t & f domain**	**MARCUS MOTZKUS**	An obituary of MARCUS MOTZKUS	26
09:00		Arnulf Materny	Ultrafast Charge-Pair Dynamics in Organic Semiconductor Devices Under the Influence of External Electric Fields	27
09:20		Michele Marrocco	The Phase Takes It All	28
09:40				
10:00		Francesco Tani	Covariance spectroscopy of molecular gases using modulational instability in hollow-core PCF	29

10:20	**Coffee Break @ Exhibition Room**			
11:00	**Chi2 NLO Spec. 1**	Ellen Backus	Structure and Vibrational Dynamics of Interfacial Ice I_h	32
11:40		Julien Rehault	Phase-sensitive Sum Frequency Spectroscopy by Time-Domain Ptychograph	34
12:20	**LUNCH**			
14:00	**INDUSTRIAL**	AMPLITUDE Gabriel Loata	High Energy & High Repetition Rate Femtosecond Laser Systems for Nonlinear Spectroscopic Applications	37
14:20		ZURICH INSTR. Claudius Riek	Maximize measurement performance for periodic signals by optimized use of lock-in amplifiers and boxcar averagers	38
14:40		TELEDYNE Norbert Gulde	Advances in camera and spectrograph technologies for low light detection	39
15:00		EKSPLA R.Januskevicius	Presentation by Exspla representative	40
15:40	**Poster Session, Exhibition, Coffee**			
17:00	**DUAL-COMB**	Nathalie Picqué	Laser frequency combs for nonlinear spectroscopy of molecules *(Webinar presentation)*	42
17:40		Oliver Hekl (Rep. by Fellinger, Jackob)	Robust and Flexible Yb:fiber Laser Source for Single- and Dual-Comb Spectroscopy Applications	44
18:00	**Day End**			
18:20	**Steering Committee Meeting**			

Tuesday September 28th 2021

08:00	**Registration**			
08:40	**Chi2 NLO Spec. 2**	Ali Dhinojwala	Understanding Acid-Base Interactions at Solid-Liquid Interfaces	46
09:20		Daria Maltseva	Interaction of the TRPML1 Ion Channel's N-terminus with Biomembranes	48
09:40		Malik Nafa	Optically rectified comb for THz-QCL precision spectroscopy	49
10:00		Imran Aslam	Unique Non-Linear White Light Emission from Combustion-Derived Particles to Develop Diagnostic Biomedical Assays	50
10:20	**Coffee Break @ Exhibition Room**			
11:00	**CARS+Other Raman**	Majed Chergui	Non-linear effects with ultrashort X-ray and optical pulses *(Webinar presentation)*	52
11:40		Jan-Christoph Deinert	Exploring nonlinear THz-driven dynamics on sub-cycle timescales at the TELBE facility: From Dirac materials to Higgs spectroscopy	54
12:00		Hanieh Fattahi	Near-Infrared Molecular Fieldoscopy	55
12:20	**LUNCH**			
14:00	**NL Spectroscopy**	Anna-Lena Sahlberg	Non-linear mid-infrared laser techniques for combustion diagnostics	58
14:40		Mikhail Shevchenko	Effective Anti-Stokes Component of Low-Frequency Raman Scattering Generation under Biharmonic Excitation *(Webinar presentation)*	60
15:00		Aleksei Smirnov	Anisotropic gold nanoparticles conjugates as a prospective tool of tumor cells imaging: study by stimulated surface-enhanced Raman microscopy	61
15:20	**Poster Session, Exhibition, Coffee**			
16:20	**Social Event and Conference dinner**			
20:00	**Day End**			

Wednesday September 29th 2021

08:00	Registration			
08:40	**CARS**	Rosa Santagata (Rep. Elodie Lin)	fs/ps-CARS spectroscopy platform for combustion thermometry and hyperspectral microscopy	64
09:20		Francesco Mazza	Ultrabroadband fs/ps coherent Raman spectroscopy behind optical windows via in-situ fs laser-induced filamentation	66
09:40		Roland Ackermann	A Study on Carbon Gasification Dynamics using Ultrabroadband Coherent Anti-Stokes Raman Scattering	67
10:00		Xiaodong Zhao	Picosecond Optical Parametric Amplifier Pumped by A Thin-disk Laser at 1 µm for Coherent Anti-Stokes Raman Scattering	68
10:20	**Coffee Break @ Exhibition Room**			
11:00	**Chi2 NLO Spec. 3**	Björn Braunschweig	Remote Control of Photoswitchable Amphiphiles at Aqueous Interfaces	70
11:40		Ahmed El-Zohry	Revisiting the Redox Behavior of Gold Surfaces via Sum Frequency Generation	72
		Monika Chaudhary	Amino Acid Based Carbon Quantum Dots for Heavy Metal Ions Sensing Studied by Sum Frequency Generation Spectroscopy *(Webinar presentation)*	73
12:00				
12:20				
12:40	**LUNCH**			
14:00	**COVID-19 Extraordinary Session****			
15:00	**Closing Session**			
15:20	**Conference End**			

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Posters: September Mon 27th and Tue 28th 2021

CONTRIBUTIONS

Sunday September 26th 2021

- OPENING SESSION
- KEYNOTE

ECONOS 2020 2021
Karlsruhe

OPENING SESSION

Atmospheric Surface-Science research @ KIT (story, goals and achievements)

Ahmed Abdelmonem
Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

Water-ice-aerosol interactions in atmosphere play a big role in changes of our hydrosphere and climate. For example, heterogeneous ice nucleation on the surface of atmospheric aerosol particles is important for cloud formation and climate system. The structural and chemical characteristics of the surface of an ice nucleation particle (INP) play a major role in its ice nucleation ability. Nevertheless, this role is not well explored in terms of surface-surface interactions. Atmospheric aerosol-cloud-climate interactions (e.g. particle oxidation and photosensitization, heterogeneous ice nucleation ...) are fundamental processes in the atmosphere. Despite the importance of these processes in energy transfer, cloud dynamics, precipitation formation, and hence in climate change, little is known about the molecular mechanism and the respective contribution of different surface properties of the atmospheric aerosols and ice nuclei controlling these processes in the atmosphere. Nonlinear optical spectroscopy, particularly second-harmonic generation (SHG) and sum-frequency generation (SFG) are powerful surface spectroscopic techniques that are capable of characterizing surface and interfacial interactions on the molecular level. The author was successful to set out a new research line, Atmospheric Surface-Science (A.S.S.), in the Institute of Meteorology and Climate Research – Atmospheric Aerosol Research (IMK-AAF) at Karlsruhe Institute of Technology (KIT) through a start -up budget from the Helmholtz association and four successful grants from the German Research Foundation (DFG)*. The aim of this research is to investigate atmospheric aerosol-cloud-climate interactions on the molecular level using NLO spectroscopy. Atmospheric interactions of interest include, but are not limited to, heterogeneous ice nucleation particle oxidation and photo-sensitization, secondary aerosol and biogenic particle formation, molecular composition-, phase-, acidity- and structure- changes …). In the opening session, the A.S.S. at KIT was introduced. A scan over the story, goals and achievements to date of A.S.S. including hosting ECONOS in Karlsruhe was presented in an accompanying poster.

*Grants

1. Start-Up-Budget (STUB 2012) in 2012 from the Helmholtz association.
2. Research grant (DFG, AB 604/1-1) in 2014 from the German Research Foundation.
3. Research grant (DFG, AB 604/1-2) in 2017 from the German Research Foundation.
4. Research grant (DFG, AB 604/3-1) in 2020 from the German Research Foundation.

Invited Speaker – Sunday Keynote

Prof. Dr. Mischa Bonn

Director of Department of Molecular Spectroscopy.
Max Planck Institute for Polymer Research, Mainz, Germany.

Novel Non-linear Terahertz Spectroscopies

Mischa Bonn is a research director at the Max-Planck Institute for Polymer Research (MPIP), Mainz, Germany. He works on label-free (ultrafast) vibrational spectroscopy and microscopy of biomolecular systems and water in such systems. He received his PhD in 1996 from the University of Eindhoven for research performed at the FOM-Institute for Atomic and Molecular Physics AMOLF in Amsterdam. After postdoctoral research at the Fritz Haber Institute in Berlin and Columbia University in New York, he worked at Leiden University from 1999 as an assistant professor, and from 2002 as associate professor. In 2004 he became a group leader at the FOM-Institute for Atomic and Molecular Physics AMOLF. In 2011 he joined the MPIP. His research interests are the structure and dynamics of molecules at interfaces, and electron transfer across interfaces. Mischa has a particular interest in the molecular details of liquid and solid water. Mischa has won several prizes and awards and has published over 400 research articles.

Novel Molecular Terahertz Spectroscopies

Mischa Bonn
Max Planck Institute for Polymer Research, Department of Molecular Spectroscopy
Ackermannweg 10, 55128 Mainz, Germany

Terahertz spectroscopy, spanning the range from 0-20 THz, or equivalently, 0-660 cm-1, has been widely and very successfully used in the study of charge carrier dynamics in semiconductors [1], and gas-phase spectroscopy. There have been decidedly fewer successful studies reporting molecular spectroscopy in condensed phases. This lack occurs despite the interest in this so-called fingerprint region of the infrared spectrum, where optical phonons and low-frequency vibrational modes are active. These modes are important, since at room temperature substantial thermal excitation of these low-frequency modes typically occurs, determining the structural dynamics in a variety of systems.

Here, I describe our recently developed new types of terahertz spectroscopies to obtain important insights in both phonon dynamics in solid-state materials [2] and coupling between high-frequency modes and low-frequency modes in water [3] and other systems.

Using strong, non-linear excitation of Terahertz modes in hybrid organic-inorganic perovskites, we reveal which low-frequency phonon mode is responsible for the anomalous blueshift of the bandgap of these materials with increasing temperature. Coherent excitation of the 1 THz mode gives rise to picosecond oscillations in the material's optical response, thereby directly identifying that this mode couples very effectively to the band gap. [2]

Elucidating coupling between different degrees of freedom in condensed matter is one of the most fundamental and challenging topics in physics and chemistry. The development of two-dimensional infrared, Raman and terahertz-Raman spectroscopies have enabled the study of the coupling between energetically close vibrational motions in mid- and far-infrared frequency ranges. Here we present a novel, Raman-based, two-dimensional terahertz-infrared vibrational (2D TIRV) spectroscopy. This new technique enables the study of coupling between the high-frequency intramolecular (HFM) and low-frequency intermolecular (LFM) motions. The technique relies on the double-resonant (THz and IR) enhancement of sum-frequency generation of THz, IR and visible laser pulses. Here, we report the use of this 2D TIRV spectroscopy to measure the coupling between the LFM and O-H stretch vibrations in the liquid water. [3]

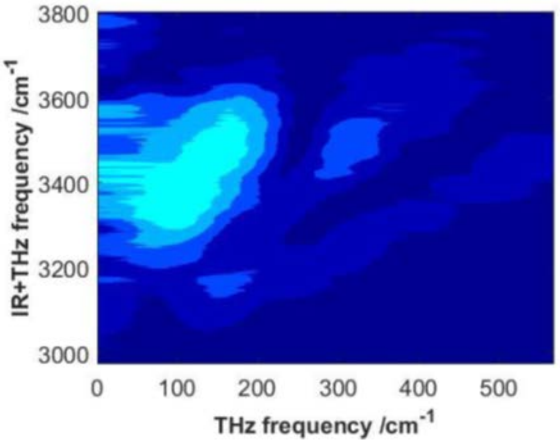

Figure 1 2D TIRV spectrum for 4 M NaCl in H_2O, revealing strong coupling between the high-frequency OH stretch mode (vertical axis) and the low-frequency hydrogen bonding modes (horizontal axis).

References

[1] R. Ulbricht, E. Hendry, J. Shan, T.F. Heinz, M. Bonn, Carrier dynamics in semiconductors studied with time-resolved terahertz spectroscopy, Rev. Mod. Phys. 83 (2011) , 543.
[2] H. Kim, J. Hunger, E. Cánovas, M. Karakus, Z. Mics, M. Grechko, D.Turchinovich, S.H. Parekh, M. Bonn, Direct observation of mode-specific phonon-band gap coupling in methylammonium lead halide perovskites Nat. Commun. (2017), DOI: 10.1038/s41467-017-00807-x
[3] M. Grechko, T. Hasegawa, F. D'Angelo, H. Ito, D. Turchinovich, Y. Nagata, M. Bonn, Coupling between intra- and intermolecular motions in liquid water revealed by two-dimensional terahertz-infrared-Raman spectroscopy, Nat. Commun. (2018), DOI: 10.1038/s41467-018-03303-y.

Monday September 27th 2021

Session 1

MARCUS MOTZKUS

This session is dedicated to our friend and colleague, Marcus Motzkus who has left us On January 5, 2020. He has contributed a lot to our scientific community.

OBITUARY FOR MARCUS MOTZKUS

On January 5, 2020, our dear friend and colleague Marcus Motzkus passed away. Marcus was a warmhearted, positive and optimistic person, who felt and shared a lot of joy in life and in science always with love to the detail. To our community he was known as an eager researcher and passionate spectroscopist. His big scientific love were the Raman- and CARS-spectroscopy. He helped shape “femto-chemistry,” from which CARS-microscopy as a new research direction arose. His academic interests were not only dedicated to natural sciences, but also to history, architecture, and music. He shared this enthusiasm with his wife Elke. For visitors to Berlin, Marcus turned out to be an extreme competent guide. Same goes for his passion for riding a bike. Crossing the alps with his children were challenges, which he loved; level country was for him, as in science, not enough.

Marcus was born in February 6, 1966 in Berlin where he also grew up, the former research lab for electron physics right next door. Marcus was fascinated by the building with his history, and already in school showed great interest in science. He first studied geophysics and geology at the Technical University of Berlin, then continued with physics at RWTH Aachen. For his doctoral thesis he went to the Max-Planck's institute for quantum optics, where he came into contact with four-wave mixing spectroscopy. As postdoc he did research in the field of femtosecond spectroscopy with the pioneer in this field, the Nobel-Prize laureate Ahmed Zewail at the California Institute of Technology in the USA. After having returned to Germany, from 1996 to 2003 he led a research group at the MPI for quantum optics in Garching where in 2002 he obtained his Habilitation from LMU Munich based on his work on coherent control of quick to extremist molecular quantum phenomena. During these years he laid the foundation for his career in the field of optimal control. His group belonged to the first ones, who successfully used modulated femtosecond laser pulses for the control of molecular processes. With highly cited publications about the optimum coherent control and impressing applications in the biophysical area, Marcus substantially contributed to the establishment of this field in Germany. Unforgotten are the "Optimal Control Workshops" on Castle Ringberg, which found a lot of attention nationally as well as internationally. They were the origin of many new ideas. According to his nature, Marcus also set high standards in the organization of the workshops. He left nothing to chance. Supreme Priority was given to the well-being of the participating scientists. All enjoyed the well-coordinated, innovative scientific program and also the pleasant atmosphere during the conference and the social events. In 2003, Marcus Motzkus followed a call to the University of Marburg. During that time, he concentrated on CARS microscopy. Finally, he was appointed W3 Professor of Physical Chemistry at the University of Heidelberg in 2009. In Heidelberg, Marcus applied his expertise in the fields of femtosecond spectroscopy and CARS microscopy to materials science. His contributions to the detailed and quantitative investigation of ultra-fast photophysical energy- and charge-transfer processes in novel organic semiconductor materials set standards for the modern interdisciplinary materials research. At the same time, he never lost his interest in elementary processes in chemical and biophysical systems. An example is his work on the characterization of real-time dynamics of synthetic photo-switchable DNA components. Through his involvement in the German Physical Society, where he had headed the Molecular Physics Group, Marcus has consistently and constantly helped the physics location Germany and therefore deserves credit. To many of us he had not only been a colleague but also a dear friend who has attended many ECW and ECONOS conferences. Due to his severe illness, he already was not able to participate in the last ECONOS. His way to early death is a painful loss for all of us. We will always remember Marcus as valued colleague, outstanding scientist and dear friend.

Ultrafast Charge-Pair Dynamics in Organic Semiconductor Devices Under the Influence of External Electric Fields

Debkumar Rana, Patrice Donfack, Vladislav Jovanov, Veit Wagner, Arnulf Materny

Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

*This contribution is dedicated to our friend and colleague, **Marcus Motzkus** who has left us far too soon. He has contributed a lot to our scientific community. We will not forget you!*

The function of semiconductor devices is based on the interaction of charges with electric fields. In some cases, internal electric fields determine the fate of generated charges and/or charge pairs; in others, external fields are applied, which take control of the processes. In our work, we have studied the influence of electric fields on the dynamics of photo-generated charge pairs by applying external electric fields, which either increase an existing internal bias or compensate it.

The generation and decay mechanisms of polaron pairs in organic semiconductor-based optoelectronic devices have to be investigated under operational conditions in order to better understand realistic processes. The initially generated charge pairs and their fate will determine the photophysical processes affecting the device performance. The occurrence of a polaron pair introduces an intermediate step in exciton dissociation into fully separated charge carriers. The role played by static electric fields in these dynamics is important, but poorly understood or not investigated in detail.

In our work [1, 2], we have investigated the ultrafast dynamics of photo-generated polaron pairs in neat poly(3-hexylthiophene-2,5-diyl) (P3HT) thin films and P3HT films sandwiched between electrical contacts with an applied external static electric field using femtosecond pump–probe transient absorption spectroscopy. Asymmetric contacts result in P3HT devices with application-related diode characteristics. We show that polaron-pair dissociation into charge carriers occurs in the P3HT device more significantly with increasing reverse bias. This is consistent with the electric field-induced dissociation of oppositely charged species. The process follows an initial instantaneous polaron-pair photo-absorption quenching caused by a pronounced immediate loss of primary photoexcitation species (hot excitons).

Furthermore, we show that the net-electric field present in the P3HT diode (including built-in-potential at 0 V bias) results in more complex dynamics. Compared to neat-P3HT thin films, clear differences can be seen. Besides polaron pairs directly originating from hot excitons, we observe polaron-pair formation during exciton dissociation via a field-mediated generation process, resulting in a slower contribution to the overall decay dynamics. Additionally, unlike in the external electric field-free P3HT film, bimolecular annihilation processes clearly appear as an additional loss channel when a field is applied. These have an impact on carrier generation performance in a working device.

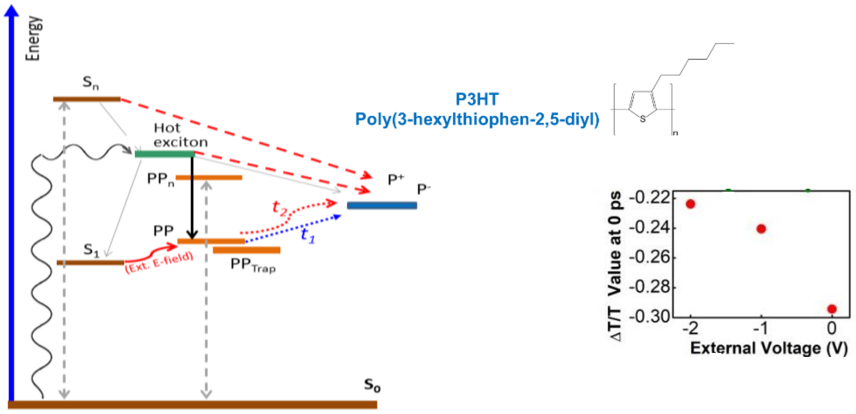

Fig. 1 Left: Scheme indicating dynamical processes induced in the P3HT organic semiconductor diode. Field-independent and -dependent generation channels for polaron pairs exist. The two contributions result in a bi-exponential decay behavior. The field-induced part shows dependence on pump intensity indicating that CT exciton formation is influenced by annihilation processes. Right: The electric field reduces the polaron-pair generation by immediate dissociation of excitons seen from the transient polaron-pair absorption at time zero.

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The Phase Takes It All

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Phase effects are fundamental in many branches of physics and nonlinear optics makes no exception. One might also go to extremes in saying that, in nonlinear optics, “the phase takes it all” (echoing the popular song “The winner takes it all” by the Swedish pop group ABBA). Indeed, if it is true that nonlinearity requires powerful light sources (hence the seemingly apt view that nonlinearity has mainly to do with amplitude effects), it is definitely phase coherence that creates the distinguished beauty and the multifaceted features of nonlinear optics. To highlight this concept in relation to the work done by Prof. M. Motzkus and his collaborators, some spectroscopic advances in the field of coherent anti-Stokes Raman scattering (CARS) are presented. These advances are picked up in the traditional research field of CARS thermometry [1-4] and from later applications to microspectroscopy [5-7]. Note that the selection is just a representation of a series of Prof. Motzkus’ works that have influenced the research of the author and other colleagues.

As to CARS thermometry, the focus is on the use of fs laser pulses to extract the thermometric information from time-domain measurements. At the time of their introduction in CARS applications to gases [1-3], they were a true novelty that was simultaneously pioneered in CARS microscopy (Xie’s group). Soon it was learnt that fs laser pulses could be effective not only for thermometry but also in highly resolved CARS measurements suitable for gaining critical information about molecular parameters [4]. Within this context, the breakthrough of chirp control to realize single-shot fs CARS thermometry deserves special mention [3].

In the second half of the talk, some relevant contributions to CARS microspectroscopy are suggested [5-7]. They have all in common the clever use of slightly different versions of the pulse shaping technique based on a spatial light modulator. First of all, attention is given to the introduction of the pulse shaper to carve specially designed phase structures in the supercontinuum spectrum generated in a photonic crystal fiber (PCF) [5]. Pulse shaping is also the key to a heterodyne CARS detection scheme where the optical fields driving the CARS process and the local oscillator are taken from a single beam of ultrashort laser pulses [6]. Finally, the technique of spectral focusing meant to have overall command over the spectral phase and amplitude of the pump, Stokes and probe pulses is briefly summarized [7]. This special version of spectral focusing introduces flexible control of the laser frequencies at the microscope enabling the possibility of multimodal imaging.

The mention of these works by Prof. Motzkus gives just a partial flavor of his relentless activity in which phase control is one of the dominant themes.

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Covariance spectroscopy of molecular gases using modulational instability in hollow-core PCF

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Low-noise ultrashort laser pulses are essential for nonlinear optical spectroscopy. As the duration gets shorter and the carrier frequency higher, however, generating pulses with sufficient peak power becomes difficult. In the x-ray spectral region, free electron lasers can deliver high energy fs pulses, which – with a few exceptions – exhibit strong stochastic fluctuations. Consequently, methods which take advantage of these fluctuations have been developed to achieve temporal resolutions beyond the average duration of the pulses and only limited by their coherence time [1–3]. Here, we report that a noisy supercontinuum (SC) generated by modulational instability (MI) can be used to measure the vibrational Raman transitions in molecular gases, in spite of large shot-to-shot variations in the spectral power distribution. In gas-filled hollow-core photonic crystal fibre (HC-PCF) pumped with μJ-level pulses, MI can generate a PHz-wide SC extending from the near-IR to the UV [4]. In the time domain, this SC consists of an incoherent train of few fs (or shorter) pulses with sufficient peak power both to pump and probe a molecular gas. By acquiring an ensemble of random spectra, information can be extracted about the sample [5]. This covariance-based technique relies on correlations between spectral components that are imprinted on the SC by the nonlinear response of the sample.

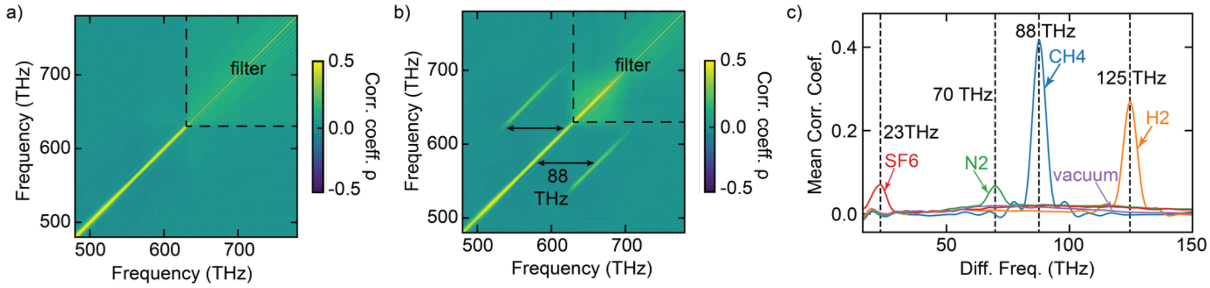

Fig. 1. (a) Covariance map for evacuated fibre and (b) for a sample with 15 bar CH$_4$. (c) Mean correlation coefficients plotted against frequency difference from the diagonal when the fibre is either evacuated or filled with a few different molecular gases at 15 bar.

The SC is generated by launching Ti:sapphire pulses (100 fs, 805 nm, 7.2 μJ, 1 kHz) into a single-ring PCF (30 μm core diameter, 25 cm length) filled with 22 bar Ar. By mean of parabolic mirrors, the incoherent pulses at the fibre output are collimated and launched into a 7-mm-long kagomé-PCF (34 μm core diameter) placed in a second gas cell containing the sample gas. The length is kept as short as possible so as to suppress the effect of (weaker) instantaneous nonlinearities, which introduce frequency correlations. The pulses emerging from the kagomé-PCF are delivered to a spectrometer, triggered to capture the single-shot spectra of individual pulses. A long pass filter (cut-off 495 nm) is placed before the second fibre to introduce a sharp edge in the spectrum, serving to enhance the covariance signal.

Fig. 1 shows the covariance maps obtained by calculating the Pearson coefficients of an ensemble of 15,000 random spectra recorded at the output of the second fibre when it was (a) evacuated and (b) filled with 15 bar CH$_4$. In the latter case, clear lines appear (parallel to the diagonal) that correspond to non-zero correlations caused by induced Raman coherence in the medium. The line-plots in Fig. 1(c) correspond to the mean correlation coefficient, calculated across the frequency range over which the lines appear in the covariance maps, plotted as a function of the frequency separation from the diagonal. The purple curve corresponds to the data from Fig. 1(a) for an evacuated PCF and has no peak. The other curves correspond to the data obtained when the fibre was filled with 15 bar of one of the following gases: SF$_6$, N$_2$, CH$_4$, H$_2$. Each curve has a clear peak at the frequency corresponding to the vibrational Raman shift of the probed gas.

These results show that MI-driven supercontinua can be used effectively for femtosecond covariance spectroscopy of molecular gases. The detection sensitivity can be significantly increased by increasing the stochastic fluctuations, and by acquiring a larger number of spectra. The technique is broadband, not limited to the detection of Raman shifts, and can be easily extended to the deep and vacuum ultraviolet, where realizing low noise sources of few fs pulses is considerably more difficult.

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Monday September 27th 2021

Session 2

χ^2 Spectroscopy 1

Invited Speaker

Prof. Dr. Ellen Backus

Professor of Physical Chemistry
Faculty of Chemistry, University of Vienna, Austria.

Water at interfaces probed by sum frequency generation spectroscopy

Since October 2018 Ellen Backus is professor for physical chemistry at the University of Vienna. After her chemistry studies at the University of Amsterdam and her PhD studies at Leiden University, she moved in 2006 to the University of Zurich for her postdoctoral work. In 2008 she joined AMOLF Institute in Amsterdam on a independent PostDoc fellowship. In 2012 she moved to Mainz to become a groupleader at the Max Planck Institute for Polymer Research followed by an independent Minerva groupleader position at the same place. Her research focuses on the structure and dynamics of water at interfaces.

Structure and Vibrational Dynamics of Interfacial Ice I_h

Prerna Sudera[1], **Mischa Bonn**[1], **Ellen H.G. Backus**[1,2]

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The dynamics of vibrational energy relaxation and dissipation at the surface of aqueous systems is relevant for, e.g., chemical conversion occurring at the surface of those systems: the energy flow pathways determine the likelihood of a reaction taking place on the surface. Subtle differences in the energy dissipation mechanism for liquid and solid water can possibly account for the different (photo-)chemical activities of water and ice surfaces, relevant for atmospheric processes.

Here, we exploit surface-specific ultrafast vibrational spectroscopy to elucidate the vibrational dynamics of both hydrogen-bonded and non-hydrogen bonded water molecules at the surface of solid water. We compare the results to liquid water in an attempt to understand molecular-level differences in interfacial water in the two states. To study water in its solid form, we grow single-crystalline hexagonal ice I_h and investigate the basal plane.

We used a femtosecond infrared excitation pulse to excite the O-H stretch vibration of water molecules, and probe the effect of that excitation with sum-frequency generation (SFG) spectroscopy. Being a second-order nonlinear process, SFG is surface-specific, and hence, it is well-suited to study the vibrational dynamics of specifically surface molecules. In addition to its molecular specificity, SFG is also sensitive to molecular order and orientation. Moreover, the vibrational frequency of the O-H stretch vibration provides information about the surrounding of the water molecule.

In detail, we excite water and ice at ~3100 and ~3300 cm^{-1}, the low- and high-frequency regions of the water stretch band and probe subsequently the effect of the excitation over the entire O-H stretch region. Our results show extremely rapid spectral diffusion for both ice and water on sub-100 fs timescales, before vibrational relaxation and thermal redistribution of excess energy on several 100’s of fs timescales. The fast dynamics in ice could potentially be explained by proton ordering at the interface.

We compare the observed relaxation dynamics of water molecules at the surface of single-crystalline ice with that at the water-air interface and discuss the potential implications of the results for chemical dynamics at the two surfaces.

Phase-sensitive Sum Frequency Spectroscopy by Time-Domain Ptychography

Julien Réhault[1], *Priscila Cavassin*[1], *Bruno G. Nicolau*[1]
and Natalie Banerji[1]
1. University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

Phase-Sensitive Sum-Frequency Generation Spectroscopy (PS-SFG) permits the measurement of both real and imaginary part of the surface second order susceptibility $\chi^{(2)}$ [1]. Experimentally, in the broadband scheme of SFG [2], it is to our knowledge always achieved by heterodyning, i.e. mixing the SFG signal with a local oscillator and monitoring the spectral interference, so that the phase is determined relative to a known reference.

In this contribution, we show that it is possible to perform vibrational PS-SFG without heterodyning. To this purpose, we applied to SFG a recently demonstrated technique of ultrashort pulse characterization named time-domain ptychography [3] (TDP). In TDP, a long and well characterized probe pulse is mixed with the unknow pulse in a second order mixing crystal and a series of SFG spectra are measured for different delays between the probe pulse and the signal. With the constraint that the delay spacing is shorter than the probe duration (FWHM), it is possible to apply the ptychographic iterative engine (PIE) to recover unambiguously the phase and amplitude of the unknow pulse from the recorded spectra.

Applying this idea to SFG, we could first show theoretically that it is possible to determine the real and imaginary part $\chi^{(2)}$.For a proof of concept, we used as a probe pulse a long time-asymmetric pulse created by passing a femtosecond pulse through a Fabry-Perot etalon. We tuned the frequency of the infrared pulse to the CH stretch region and studied a monolayer of 1-Octadecanethiol (ODT) on gold [2].

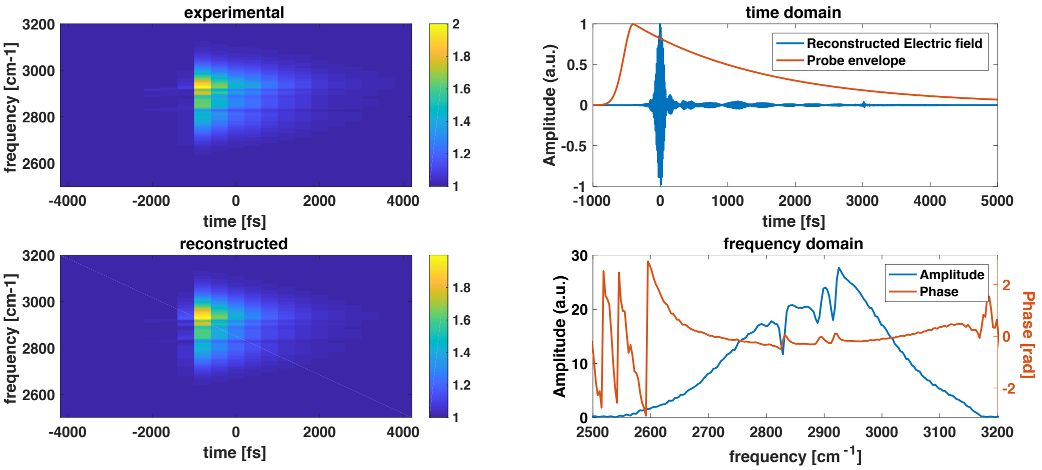

Fig 1. a) and b) are 2D plot of the signals at different delays and the reconstruction with the PIE algorithm, respectively, the time step was set to 400fs. Fig.1 c) displays the envelope of the probe pulse and the reconstructed SFG signal. Fig.1 d) displays the amplitude and phase of the reconstructed signal, which is dominated by the strong non-resonant background (NRB) of gold but the complex spectral signature of ODT are clearly resolved.

We will show our preliminary results (Fig 1) and discuss the advantages and drawbacks of TDP applied to VS-SFG.

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Monday September 27th 2021

Session 3

Industrial

High Energy & High Repetition Rate Femtosecond Laser Systems for Nonlinear Spectroscopic Applications

Gabriel Loata

Amplitude Laser

Maximize measurement performance for periodic signals by optimized use of lock-in amplifiers and boxcar averagers

Claudius Riek[1]
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Identifying minute changes in an observed signal is crucial in photonic measurements such as pump-probe spectroscopy, dual comb spectroscopy, or electro-optic sampling of phase-stable pulses. These periodic signal components are often covered in noise, so that proper recovering techniques are necessary. The chosen method has to average out spurious fluctuations of the detected physical variable while accumulating all available signal power to provide the best possible signal-to-noise ratio (SNR) for the acquired data. Importantly, this choice is not specific to a certain scheme but rather depends on the individual implementation of an experiment. It is a function of multiple parameters such as signal shape, duty cycle, and the noise background

For example, the modulation imprinted by a chopper wheel on a laser beam depends on the ratio between the beam diameter and the aperture of the chopper wheel. If their sizes are similar, the modulation is close to sinusoidal and all signal power is contained in the first harmonic. If the laser beam is much smaller, however, one obtains a close-to-rectangular modulation in which the signal power is spread over multiple harmonics in the frequency domain. In the first case, a lock-in amplifier can be used efficiently. In the second scenario, a boxcar averager may be a better fit.

This rather simple example illustrates how lock-in amplifiers and boxcar averagers offer complementary approaches to the recovery of the best SNR for periodic signals. Nonetheless, signals such as the one illustrated in Fig. 1 a) represent less obvious cases. This particular signal comes from balanced photodetection of two adjacent Raman pump pulses [1], one with simultaneous Stokes excitation and the other without. The resulting modulation – at half the repetition rate – was analysed with both lock-in demodulation and boxcar averaging. The shaded areas indicate the chosen boxcar windows. The relative noise ratio (RNR) between the two measurements is depicted in Fig 1b) as a function of the integration time of the boxcar relative to the fixed lock-in measurement duration. In this example, at less than half the integration time it is already clear that the boxcar averager brings an advantage.

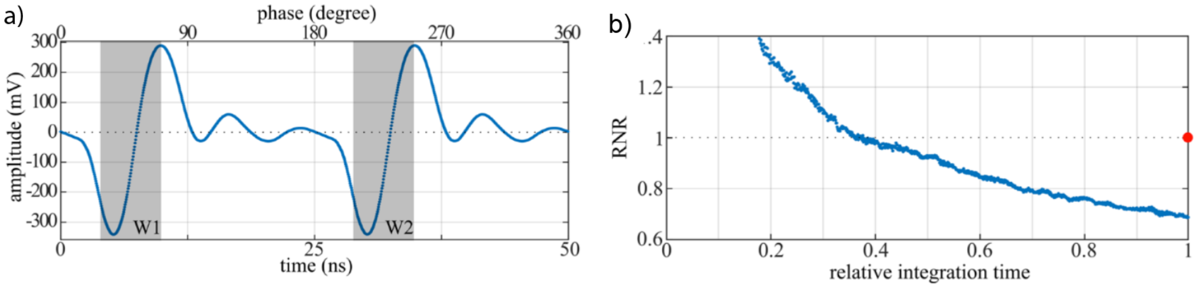

Fig. 1 Voltage signal **a)** from a balanced photodetector depicted over time (bottom axis) and phase (upper axis) of one modulation period. It represents two Raman pump pulses with simultaneous Stokes excitation on one of the pulses. The shaded areas (W1 and W2) indicate the boxcar integration windows. The relative noise ratio **c)** between boxcar and lock-in measurement is depicted as a function of boxcar integration time relative to 10 time constants of the lock-in amplifier. From [1].

In general, different measurement parameters such as modulation frequency, window width, averaging periods, time constant, and filter order form a multi-dimensional parameter space; in this sense, all of these parameters influence the choice of the best signal recovering approach. We will provide a guide on how to identify the best measurement technique and how to choose the associated parameters to achieve maximum SNR. Since the attainable SNR has a direct consequence on the smallest measurable change in the signal or the required measurement time, making informed choices will help to measure tiny signals as fast as possible.

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Advances in camera and spectrograph technologies for low light detection

Norbert Gulde
Teledyne Princeton Instruments

Details will be presented about the scope of Teledyne Princeton Instruments technology that is used in research from x-ray to the NIR/SWIR regions for a wide range of scientific research applications. Description of why the specific technologies are required for specific types of research will be discussed as well as the breadth of products including CCD, ICCD, CMOS, and InGaAs cameras, as well as spectrographs.

High spectral resolution picosecond and femtosecond SFG spectrometers

Regimantas Januškevičius[1]***, Robertas Kananavičius***[1]***, Vitalij Kod***[1]***, Udo Umhofer***[2]***, and Gediminas Niaura***[3]

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3. *State research institute Center for Physical Sciences and Technology, Savanorių 231, LT-02300 Vilnius, Lithuania*

Sum frequency generation (SFG) spectrometres are reliable nonlinear spectroscopic tools. New picosecond and femtosecond SFG spectrometres are presented.

Our picosecond and femtosecond SFG spectrometres have same property – high spectral resolution. The main features and properties of picosecond and femtosecond spectrometres are compared and discussed.

Ekspla provides complete sum frequency generation spectrometres ready for measurements. The picosecond SFG spectrometer developed by Ekspla scientists and engineers is a nonlinear spectrometry instrument, convenient for everyday use. The picosecond Ekspla SFG spectrometre a reliable workhorse with a broad spectral region, automatically tuned from 1000 (625) to 4300 cm^{-1}, a high spectral resolution (2 or 6 cm^{-1}), and motorised control of polarization optics [1]. Higher laser repetition rate, better signal-to-noise ratio, faster monochromator and additional accessories make measurements faster.

For new femtosecond SFG system realisation we created optically coupled two-channel laser system which generates narrow-band (~1.5 cm^{-1}) visible and broadband mid-IR pulses [2]. We have achieved a high spectral resolution and a high energy of the visible channel which is limitted only by sample damage threshold.

Ekspla is a laser manufacturer from Vilnius, Lithuania, designs and manufactures advanced lasers and systems. Its main competence is the ability to effectively tailor products for specific applications and requirements. The main products are pulsed femtosecond, picosecond, nanosecond lasers and tunable wavelength systems for scientific and industrial application, spectroscopy systems, and high-intensity laser systems.

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Monday September 27th 2021

Session 4

Dual Comb

Invited Speaker

Webinar speaker

Dr. Nathalie Picqué

Max Planck Institute of Quantum Optics, Germany

Nonlinear broadband spectroscopy with laser frequency combs

Nathalie Picqué is a senior research scientist at the Max-Planck Institute of Quantum Optics (MPQ), Garching near Munich, Germany. She obtained her doctoral degree in 1998 and her habilitation in 2006, both from the Université de Paris-Sud (Orsay, France). After a post-doctoral stay at the European Laboratory for Nonlinear Spectroscopy (Florence, Italy), she was appointed as a permanent research scientist with the Centre National de la Recherche Scientifique (CNRS) in 2000. In 2011, she moved her laboratories to the MPQ.

Dr. Picqué's research interests focus on molecular physics, precision spectroscopy and laser technology. She launched her research activities towards broadband molecular spectroscopy with optical frequency combs around 2005 simultaneously and independently to two or three other groups outside Europe. The techniques that she has been pioneering are now attracting the interest of many other groups are moving towards such spectroscopy in order to realize accurate, fast and miniaturized spectroscopic tools for different applications, ranging from fundamental research in molecular physics to bio-molecular imaging and medical diagnostics. With her group, Dr. Picqué continues to advance the frontiers of laser frequency combs and molecular spectroscopy. For her work, Nathalie Picqué has already received many prizes and awards including the 2007 Bronze Medal of the CNRS (best young scientist of the year in the field "Optics and Lasers, Atomic and Molecular Physics, Hot Plasmas" in France), the 2010 Beller Lectureship Award (American Physical Society), the 2013 Coblentz award (Coblentz Society) and the 2019 fellowship of the Optical Society.

Laser frequency combs for nonlinear spectroscopy of molecules

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A frequency comb is a broad spectrum of evenly-spaced phase-coherent narrow laser lines. Initially invented for frequency metrology, such combs enable new approaches to spectroscopy over broad spectral bandwidths, of particular relevance to molecular spectroscopy [1].

One of these approaches, dual-comb spectroscopy, enables fast and precise measurements over broad spectral ranges at any spectral resolution. High-accuracy determination of all spectral line parameters [2] and broadband detection in light-starved conditions [3] become possible. Moreover, since laser frequency combs often involve intense ultrashort laser pulses, nonlinear interactions can be harnessed. This opens up new opportunities for precision spectroscopy and stringent comparisons with theories in atomic and molecular physics. In the mean time, progress towards chip-scale dual-comb spectrometers promise integrated devices for real-time sensing in analytical chemistry and biomedicine. Multiplex accessing of hyperspectral images may dramatically expand the range of applications of nonlinear microscopy.

With selected examples, I will illustrate the rapidly-advancing field of dual-comb spectroscopy.

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Webinar presentation

Robust and Flexible Yb:fiber Laser Source for Single- and Dual-Comb Spectroscopy Applications

Aline S. Mayer[1], Jakob Fellinger[1], Wilfrid Grosinger[1], Georg Winkler[1], Lukas Perner[1], Sarper Salman[2,3], Stefan Droste[2], Chen Li[2], Christoph M. Heyl[2,3], Ingmar Hartl[2], Oliver H. Heckl[1]

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[2]Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany
[3]Helmholtz-Institute Jena, Fröbelstieg 3, 07743 Jena, Germany

The development of low-noise mode-locked fiber lasers for frequency comb applications has tremendously progressed over the past years [1]. Recently, all-polarization maintaining (PM) designs based on a nonlinear amplifying loop mirror (NALM) with a non-reciprocal phase bias [2], also termed "figure-9" laser, have gained attention due to their robustness and reliable self-starting mode-locking operation.

Here, we demonstrate a particularly flexible ytterbium (Yb)-based design (Fig. 1 (a)) that both allows for "traditional" mode-locked operation with a single-pulse-train/single-comb output (Fig. (b), (c)), as well as dual-comb operation (Fig. (d), (e)), where two pulse trains with a small difference in repetition rate Δf_{rep} are simultaneously emitted. Dual-comb operation is obtained via spectral subdivision using a simple tuneable mechanical beam block. Both in the single- and dual-comb configuration, mode-locking can be obtained at different values of intra-cavity group delay dispersion (GDD), which allows to tune the optical output spectra, but also impacts the comb noise properties. Using the slit-method described by Knox [3], we measured the total intracavity dispersion for different grating separations and analyzed the noise properties (amplitude noise, timing jitter and comb offset noise; data not shown in figure). We found that operating far from the spontaneous emission peak of Yb (~1030 nm), but close to zero intracavity dispersion, strongly reduces the influence of pump noise and hence results in narrow comb-lines. In dual-comb operation, these favourable noise properties along with common-mode noise cancelation allowed measuring the transmission of a 5-mm thick zinc selenide (ZnSe) etalon using a simple photodiode connected to an oscilloscope with the laser completely free-running. This Yb-based platform can easily be combined with power scaling stages and subsequent nonlinear wavelength conversion. Therefore, the reported platform shows great potential as a versatile tool for many applications in spectroscopy and beyond.

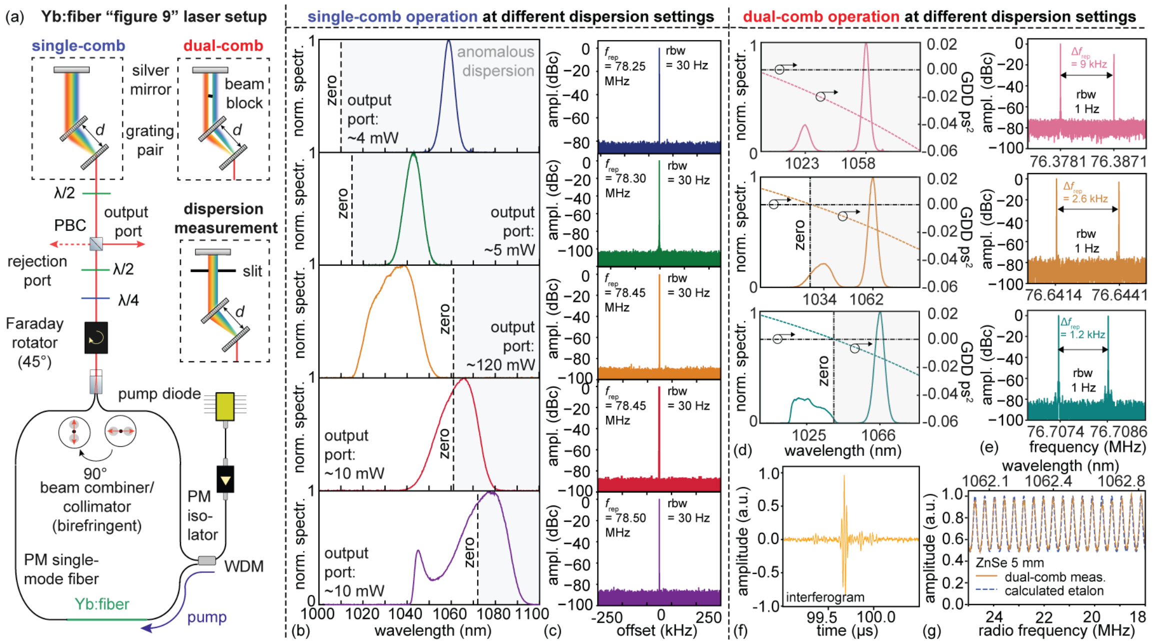

Fig. 1 (a) Laser setup depicting the single- and dual-comb operation mode as well as the slit-method used for intra-cavity dispersion measurements. (b) Optical spectra of modelocking states obtained in single-comb operation at 5 different grating separations *d* and (c) corresponding measurement of the repetition rate frequency f_{rep}. (d) Optical spectra in dual-comb operation at 3 different grating separations and (e) corresponding measurement of the repetition rate frequencies $f_{\mathrm{rep},1}$ an $f_{\mathrm{rep},2}$. (f) Single-shot time domain interferogram of the configuration with Δf_{rep} =2.6 kHz corresponding to (g) transmission measurement of a 5-mm thick ZnSe (orange). The simulated etalon transmission is shown in dashed blue for comparison.

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Tuesday September 28th 2021

Session 1

χ^2 Spectroscopy 2

Invited Speaker

Prof. Dr. Ali Dhinojwala

University of Akron, USA

Understanding Acid-Base Interactions at Solid-Liquid Interfaces

Dhinojwala holds a BTech in Chemical Engineering from the Indian Institute of Technology and a PhD in Chemical Engineering from Northwestern University. He currently serves as Interim Dean of the College of Polymer Science and Polymer Engineering, and Professor of Polymer Science at UAkron. Dhinojwala's research interests include adhesion, friction, and wetting, as well as structural color. Member of his lab developed novel spectroscopic techniques for understanding the physical properties of molecules at surfaces and interfaces, as well as synthetic adhesives inspired by geckos and spiders.

Understanding Acid-Base Interactions at Solid-Liquid Interfaces

Ali Dhinojwala, Saranshu Singla, Michael Wilson, Nityanshu Kumar, Sukhmanjot Kaur, and Nathaniel Orndorf
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Interfacial interactions govern a number of macroscopic behaviors including adsorption and self-assembly. Acid−base interactions have previously been shown to comprise a significant portion of the interaction strength for polar liquids in contact with high-energy solids. In my talk, I will present how we are using interface-sensitive sum frequency generation spectroscopy to monitor the frequency shift of sapphire surface hydroxyl groups in contact with liquids to independently determine the Drago−Wayland acid−base parameters.[1-7] We have used a wide variety of liquids and polymers to characterize the shift in frequency of surface hydroxyl groups and relate this shift to the strength of the enthalpic interactions. The frequency shift of sapphire surface hydroxyl groups correlates with the Drago−Wayland acid−base parameters, highlighting the connection between interfacial interactions and interactions of molecules dissolved in solution. The acid-base interactions help us in understanding segregation of liquids at solid-liquid interfaces [4], segregation of polymers in blends [2], adsorption of polymers [3], and the strength of adhesive interactions [7]. The wide application of frequency shift and Drago−Wayland acid−base parameters for the characterization of interfacial acid−base interactions has important implications for various fields including chemistry, biology, and engineering.

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Interaction of the TRPML1 Ion Channel's N-terminus with Biomembranes

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The N-terminus of the transient receptor potential mucolipin 1 (TRPML1) ion channel is partly disordered and usually not reported in the available TRPML1 cryo-EM structures [1]. It contains binding sites for PI(4,5)P_2 (plasma membrane lipid) and PI(3,5)P_2 (lysosomal lipid) [2]. We test the influence of negatively-charged phospholipids on the secondary structure formation of the N-terminus by forming monolayers at the air/buffered aqueous solution interface. The data suggest a predominantly α-helical structure and orientation at the interface which is enhanced in presence of negatively charged lipids. We also obtain information on the effect of the peptide binding on the order in the phospholipid monolayer and observe that the adsorption of the peptides also clearly affects the phospholipid headgroup and only slightly the tails.

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Optically rectified comb for THz-QCL precision spectroscopy

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The terahertz (THz) domain, ranging from 0.1 to 10 THz has been for a long time a hard-to-access and thus an underexploited spectral region. Different techniques have been developed to explore molecular transitions in this region. In the time-domain, Asynchronous Optical Sampling (ASOPS) spectroscopy provides broadband spectroscopy from 0.13 to 3.35 THz [1], with resolutions down to $6\cdot10^{-8}$ [2], at the cost of acquisition times of several minutes. In the frequency domain, the techniques are mainly based on second order frequency conversion setups. A major inconvenient for these approaches is the low optical power (~ 1 µW) available for spectroscopy. This issue can be overcome by THz Quantum Cascade Lasers (QCLs), semiconductor-based laser sources allowing ad-hoc tailoring of their emission frequency (single-mode, multi-mode, frequency comb), and which optical power in continuous wave operation is in the mW range [3].

Moreover, THz QCLs have shown a very narrow intrinsic linewidth (in the order of ~100 Hz) [4], that can be achieved by phase-locking the device emission to a reference local oscillator. In our case, the reference local oscillator is a THz frequency comb generated by optical rectification of a fs-laser (OR-comb). The heterodyne detection is performed through a Hot Electron Bolometer (HEB), allowing efficient detection of the down-converted radio-frequency beatnote between a few percents of the QCL emission and one mode of the THz OR-comb. This heterodyne signal can be used on different purposes, with single-mode and frequency comb QCLs. One purpose is phase-locking of a single mode QCL, shrinking the spectral emission to its intrinsic linewidth, while almost all the QCL optical power remains available for absorption spectroscopy [5]. Besides, phase-locking has been performed as well on a THz-QCL frequency comb, permitting its full stabilization and its thorough caracterization [6]. Another purpose is its application for dual-comb spectroscopy, combining the advantages of both QCL- and OR-comb - respectively high power per tooth, and an absolute frequency scale referenced to a primary frequency standard. Concretely, Fig. (a) illustrates the scanning of the frequencies covered by the QCL-comb teeth, that enables retrieval of rotational CH_3OH transitions as shown on Fig. (b). Such spectra present a robust absolute frequency calibration, and the linecenter in vacuum can be determined with a relative precision of $6\cdot10^{-8}$ [7]. The latter can be improved in the future by performing acquisitions with a fully phase-locked QCL comb.

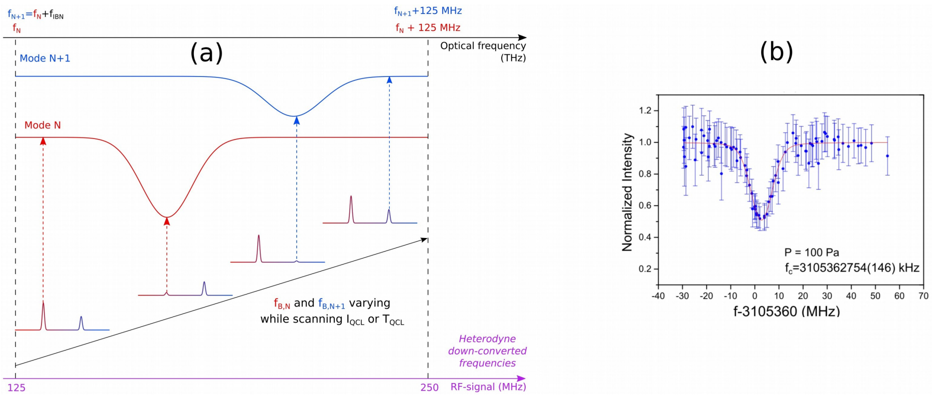

Fig. Multi-heterodyne detection on a QCL frequency comb : (a) Schematic representation* ; (b) Application on the CH_3OH rotational transition (J, K) = (11, 11 → 12, 12), acquired at a pressure of 100 Pa.
* Frequencies of two consecutive modes N (red) and N+1 (blue) are tuned by driving current or heat sink temperature variations. This tuning corresponds to variations in the down-converted heterodyne beatnote (HBN) signals, respectively $f_{B,N}$ and $f_{B,N+1}$, whose amplitude are continuously monitored. The retrieval of the variations in the HBN amplitudes allows simultaneous reconstruction of molecular transition that are spaced by the intermodal beatnote f_{IBN} in the THz frequency domain.

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Unique Non-Linear White Light Emission from Combustion-Derived Particles to Develop Diagnostic Biomedical Assays

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Combustion-derived particles (CDPs) such as carbonaceous particulate matter (PM) are of high interest to scientists worldwide because of their toxic effects on human health. Hence, there is an increasing need to detect and quantify these particles to understand their toxicity. Among different techniques, absorption photometry and laser-induced incandescence are commonly employed to measure CDP concentrations in gaseous samples. However, the detection of carbon-based nano- and microparticles in biological samples is a challenging task. Recently, we could detect CDPs in biological samples based on non-incandescence related white light (WL) emission under illumination with femtosecond (fs) pulsed near-infrared (NIR) laser light. Based on this unique WL emission, CDPs could be detected in human urine, placenta, and ivy leaf samples[1-4].

Ambient PM includes CDPs and other types of nanoparticles such as silica and metal oxides as a result of natural sources and anthropogenic activities. Hence, the presence of silica and metal oxide nanoparticles in ambient PM could interfere with the detection technique of CDPs based on WL emission. In our recent study [5], we could confirm the uniqueness of WL emitted by the CDPs under illumination with fs pulsed NIR lasers by performing measurements on CDPs and other standard nanoparticles. Hence, interference from other types of common nanoparticles based on WL emission is not expected when detecting CDPs in liquid and fixed samples. We could also confirm that this unique nonlinear WL emission manifests itself as broad Stokes and anti-Stokes radiation.

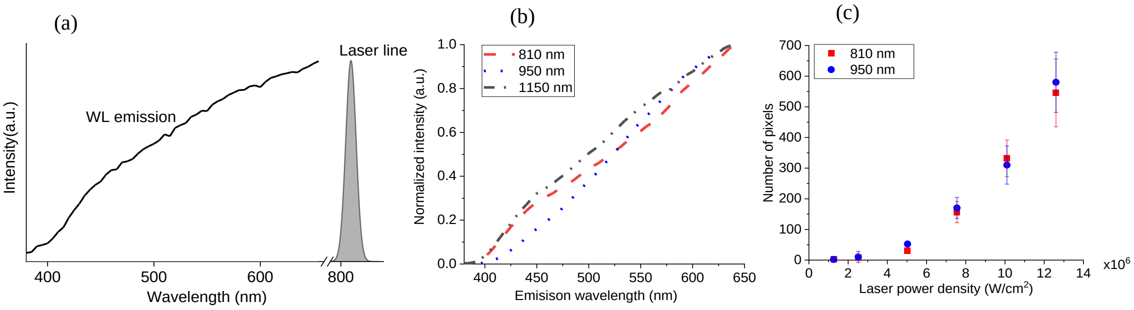

Fig. 1 (a) Unique WL emitted by CDPs covers the whole visible spectrum on the anti-Stokes side of the laser, with laser excitation at 810 nm. (b) WL emission observed from CDPs at different laser excitation wavelengths. (c) WL emission from CDPs shows a nonlinear emission response for incident laser power at laser excitation 810 and 950 nm.

Although CDPs could be detected in biological samples based on unique WL emission using laser excitation at 810 nm, we have further explored the experimental conditions to develop biomedical diagnostic assays. We could observe that the unique WL emission from CDPs is independent of the excitation laser wavelength in the NIR region such as 810, 950, and 1150 nm as shown in Figure 1b. Further, we could observe that WL emission from CDPs shows nonlinear emission response with respect to incident laser power indicating that a modest increase in incident laser power results in a substantial increase in WL emission from CDPs. This nonlinear response could be observed for excitation wavelengths in the NIR region. In addition, we have studied the effects of different concentrations of CDPs suspensions in relation to the depth of laser focus inside the suspensions. These measurements were performed in ultrapure water and biological buffer medium. We could observe that focusing depth does not have a significant effect at lower CDPs concentration. However, it becomes prominent at higher CDP concentrations. These results are a step towards the development of diagnostic, biomedical assays for the detection of CDPs.

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Tuesday September 28th 2021

Session 2

CARS and Raman Spectroscopy

Invited Speaker

Webinar speaker

Prof. Dr. Majed Chergui

École polytechnique fédérale de Lausanne , Switzerland

Non-linear effects with ultrashort X-ray and optical pulses

Majed Chergui FRSC, is professor of Chemistry and Physics at the Ecole Polytechnique Fédérale de Lausanne (EPFL) and Director of the Lausanne Centre for Ultrafast Science (LACUS). He received his BSc degree in Physics and Mathematics from Chelsea College (University of London) in 1977, his Ph.D. in Physics from the Université Paris-Sud (Orsay) in 1981 and his Habilitation from the Université Paris-Nord in 1986. He then spent six years at the Freie Universität Berlin till 1993, when he was appointed Full Professor of Physics at the Université de Lausanne, Switzerland. In 2003, he joined the Chemistry Institute of the EPFL.

Majed's research interests range from matrix-isolation spectroscopy of molecular systems to ultrafast spectroscopy of large molecules, biosystems and nanoparticles in solution, and bulk transition metal oxides. Most importantly, he is known for pioneering X-ray spectroscopy in the picosecond, then the femtosecond time domain, which he successfully applied to a wide range of scientific questions. He also made pioneering contributions to the development of ultrafast deep-ultraviolet methods, in particular 2-dimensional spectroscopy and circular dichroism. In recognition for his contributions, he received several awards and prizes among which, the Humboldt Research Award 2010, the 2015 Earle K. Plyler Award of the American Physical Society, The 2015 Edward Stern Prize for Lifetime Achievements of the International X-ray Absorption Spectroscopy Society and the 2019 Liverside Award of the Royal Society of Chemistry (UK). He is Fellow of the RSC, APS, OSA, EPS, ACA (American Crystallographic Association) as well as Foreign correspondent of the Spanish Royal Academy of Sciences.

Non-linear effects with ultrashort X-ray and optical pulses

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The past decades have witnessed a revolution in ultrafast sources, starting from optical lasers to pulsed X-rays and electron sources. Ultrafast X-ray scattering and spectroscopy are essential tools for understanding and quantifying the functionality in space and time domains of molecular and biological systems, as well as nanoscale and bulk materials.

X-ray Free-Electron Lasers (XFELs) provide intense ultrashort X-ray pulses, which in addition to enhancing the capability of existing X-ray methods such as spectroscopy (absorption, emission and resonant inelastic X-ray scattering) and scattering and diffraction, they enable novel experimental strategies, some of which involve non-linear X-ray optical phenomena, such as four-wave mixing (4WM), 2-photon absorption, X-ray second harmonic generation, etc. These unique capabilities can be harnessed to study the interplay between electronic and structural degrees of freedom in several photo-excited systems.

Here, after presenting some recent results on biological systems combining ultrafast X-ray absorption (XAS) and X-ray emission spectroscopy (XES), I will move to present recent preliminary results, that explore novel perspectives. These include ultrafast studies of chirality, the extension of ultrafast X-ray spectroscopies to non-light driven processes, and the latest development in time-resolved Resonant Inelastic X-ray Scattering paving the way for direct visualization of low energy excitations in transition metal oxides in the time domain.

Webinar presentation

Exploring nonlinear THz-driven dynamics on sub-cycle timescales at the TELBE facility: From Dirac materials to Higgs spectroscopy

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The TELBE Terahertz (THz) facility at Helmholtz-Zentrum Dresden-Rossendorf (HZDR) offers intense narrowband THz radiation for driving low-energy excitations in matter in the spectral region between 0.1 THz and 1.5 THz [1]. In combination with a pulse-resolved data acquisition scheme, we can resolve dynamics with few 10 fs time resolution and high dynamic range of up to 120 dB [2]. The combination of high field strengths on the order of 100 kV/cm and high repetition rates of up to 100 kHz make TELBE an unique facility for exploring low-energy THz excitations and *nonlinear effects* offering (resonant) access to a multitude of fundamental modes, e.g., lattice vibrations, molecular rotations, spin precession and the motion of free electrons [3]. Recently, we demonstrated THz high harmonic generation (HHG) in the model 2D material graphene [4]. Here, the ultrafast collective thermal response of free background electrons near the Dirac point [5] enables very efficient generation of harmonics in the technologically relevant THz frequency range. We further show that the underlying principle of the collective response can be generalized to other 2D and 3D Dirac materials, such as CdAs. The crucial role of doping in graphene can be exploited by, e.g. electrochemical gating, which allows tuning of the HHG efficiency by almost two orders of magnitude. The corresponding setup for phase-resolved nonlinear THz spectroscopy further enables a novel technique: Higgs spectroscopy, which offers new ways for understanding unconventional superconductivity. Using this technique, we recently discovered a new collective mode distinct from the heavily damped Higgs mode in different families of cuprates [6]. Our results establish Higgs spectroscopy as a new approach to uncover interactions directly relevant to superconductivity.

Additionally, we have begun extending the classes of examined samples from condensed matter to liquids. The implementation of a liquid jet setup at TELBE to study THz-induced birefringence has yielded the worldwide fist observation of the THz Kerr effect in a water jet. Our developments are geared toward experiments in biologically relevant systems.

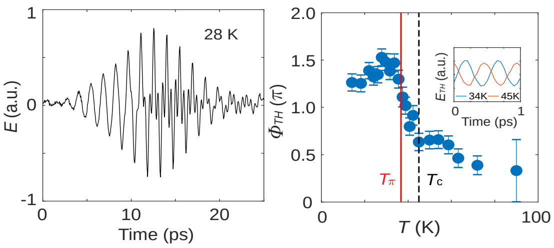

Fig. 1 Time-resolved measurement of THz re-emission in the superconductor LSCO after excitation at 0.7 THz. The 3rd harmonic becomes directly visible as oscillation of the electric field in the phase-resolved experiment (left). The temperature dependence of the phase relationship between fundamental and harmonic shows a phase jump by π at a characteristic temperature T_π. Courtesy of Stefan Kaiser, MPI Stuttgart.

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Near-Infrared Molecular Fieldoscopy

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Linear spectroscopy in near-infrared spectral range provides information on the molecular composition, structure, and conformation, affording tremendous potential for high-resolution, in-depth, label-free biological spectro-microscopy [1]. Broadband measurements in this spectral region have been carried out mainly in the frequency domain, which suffers from two limitations: i) the detection of small absorption differences is limited to the intensity noise of the source, and ii) the low detection dynamic range.

To mitigate above-mentioned limitations, we introduce the concept of molecular Fieldoscopy. In molecular Fieldoscopy, an ultrashort, phase-coherent pulse is used for molecular excitation and afterwards the transmitted complex electric field that contains the molecular response is measured directly. Here, the excitation pulse is confined to a time window of tens of femtoseconds, which is significantly shorter than molecular response. Therefore, the molecular response is detected free of background and the effect of the intensity noise of the source is eliminated. Furthermore, measuring the complex electric field allows for extracting the full spectral phase information of the molecular response, adding a new dimension to the gained spectroscopic data.

In what follows we report, to the best of our knowledge, the first field-resolved overtone spectroscopy of water molecules in liquid phase. Water has a strong $\nu_2+\nu_3$ combination band near 1930 nm (5180 cm^{-1}). 18 fs, mid-infrared (MIR) pulses centered at 2 μm were used to excite the combination band. Upon the interaction of broadband pulses with molecules, photons at the resonance frequencies are slowed down due to the increase in the refractive index and appear at the trailing edge of the excitation pulse. We aimed for the direct electric field detection of the MIR pulses and the molecular response after interaction with water molecules over several picoseconds by means of electro-optic sampling (EOS) [2].

Fig. 1 shows the measured electric field of the MIR pulses in the absence (dark blue curve) and presence (bright blue curve) of water. As can be seen, in the absence of water the amplitude of the excitation pulses goes to zero at temporal delays above 200 fs. After the injection of water, the transmitted excitation pulse is temporally chirped and the molecular free induction decay is formed which decay exponentially over 3 ps time window. Here, the molecular response can be detected free of background at temporal delays beyond 200 fs, allowing for higher detection sensitivity. Moreover, by employing broadband excitation pulses in combination with EOS the entire molecular vibrations in the fingerprint region can be simultaneously excited and detected, which holds promise for advancing femtosecond time-domain spectroscopy to direct measurement of the complex electric field and higher detection sensitivity [3].

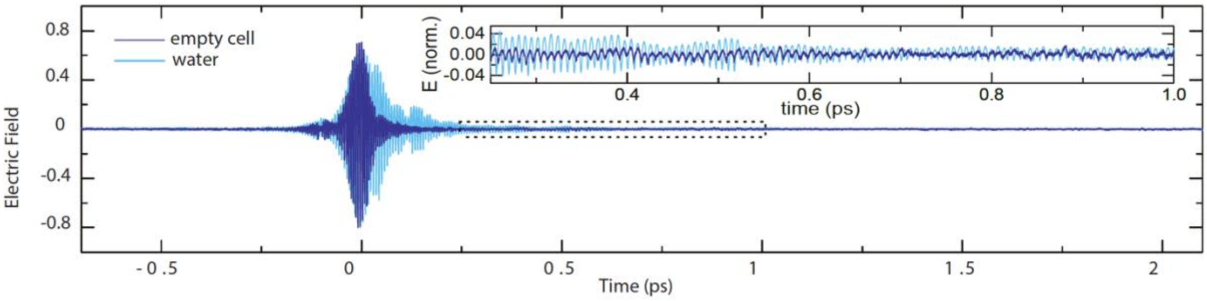

Fig. 1 The measured electric field of the MIR pulses in the absence (dark blue curve) and the presence of water (light blue curve). Inset: zoomed plot in a shorter temporal window.

Example References

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Tuesday September 28th 2021

Session 3

NL Spectroscopy

Invited Speaker

Dr. Anna lena Sahlberg

Division of Combustion Physics , Lund University

Non-linear mid-infrared laser techniques for combustion diagnostics

“Anna-Lena Sahlberg is working as Associate Senior lecturer at Lund University. She received her PhD degree at the Division of Combustion Physics at Lund University in 2016, and then worked as a Postdoc at the University of Oxford, before moving back to Lund in 2018. Her research is focused on development and application of non-linear mid-infrared laser techniques for combustion diagnostics, including laser-induced thermal grating spectroscopy (LITGS), degenerate four-wave mixing (DFWM) and polarization spectroscopy (PS).”

Non-linear mid-infrared laser techniques for combustion diagnostics

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In the past decades, non-linear laser techniques have become an important part of laser combustion diagnostic research. Non-linear laser techniques have many unique advantages, such as the high temporal and spatial resolution, high sensitivity, and the coherent nature of the signal. Employing non-linear laser techniques in the mid-infrared spectral region has many merits. Ro-vibrational transitions in the mid-infrared can be used to probe molecular species which do not have easily accessible electronic transitions. Sensitive detection down to ppm levels in harsh environments can be achieved based on the fully resonant enhancement from the strong fundamental ro-vibrational transitions. The generated coherent non-linear signal allows efficient discrimination against the strong thermal radiation from hot environments.

Degenerate four-wave mixing (DFWM) is a resonant four-wave mixing technique, which uses resonant absorption as part of the non-linear interaction between the laser beams and the medium. DFWM is a non-intrusive, sensitive technique that enables remote and zero background measurements with high sensitivity. An optical system for stable alignment of mid-infrared DFWM (IR-DFWM) has been designed [1] and applied to detection of various combustion intermediate species and pollutants, e.g. CH_4, C_2H_4, CH_3Cl, HCl, etc. and for quantitative measurements of HCN molecules in biomass combustion [2]. In addition to this, IR-DFWM excitation scans of water absorption spectra has been utilized for temperature measurements [3].

Laser-induced thermal grating spectroscopy (LITGS) is a versatile laser diagnostics technique that has been used for measurements of several physical parameters in gases [4]. In LITGS, the interference between two pulsed pump laser beams creates a periodical variation of the laser energy in the measurement point. When the pump laser beams are absorbed in the measurement point, collisional thermalization of the absorbed laser energy generates a thermal grating of periodically varying gas density along the ridges of the interference pattern, forming a laser-induced grating (LIG). Rapid density modulations in the gas creates a sound wave propagating across the LIG, causing the grating to oscillate in time. A continuous wave probe beam is aligned to cross the LIG at the Bragg angle. The signal is formed by the Bragg scattered probe beam, and the time-resolved scattering reflects the formation and time-evolution of the LIG. The oscillations in the signal offer a direct measurement of the speed of sound in the measurement point, from which it is possible to derive the temperature. LITGS offers the potential of temperature measurements with high precision. Using mid-infrared pump lasers, it is possible to utilize the strong ro-vibrational water lines for non-intrusive temperature measurements in combustion environments, where water is usually present at high concentrations.

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Effective Anti-Stokes Component of Low-Frequency Raman Scattering Generation under Biharmonic Excitation

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Using of biharmonic laser pumping, in which the frequency difference coincide exactly with the eigenfrequency of the system under study allows one to realize effective, selective and resonance excitation of this vibrational mode. Interaction of this excited mode with a pump wave can lead to effective coherent anti-Stokes generation. Coherent anti-Stokes Raman scattering (CARS) which is a nonlinear four-wave mixing process is a powerful spectroscopic tool for different molecular systems investigations. For investigation of the systems consisting of nanoscale and submicron particles coherent anti-Stokes low-frequency Raman scattering (CALFRS) experimental set up is realized.

Low frequency Raman scattering (LFRS) is an inelastic scattering of electromagnetic radiation on acoustic vibrations of nano- and submicrometer particles and as any other type of spontaneous scattering has its stimulated analogue – stimulated low frequency Raman scattering (SLFRS) [1]. The frequency shift of scattered radiation at the process of LFRS (and SLFRS) is defined by the particle morphology and is in the range from several GHz to THz for various systems. In our study for CALFRS experimental realization SLFRS is used as biharmonic pump.

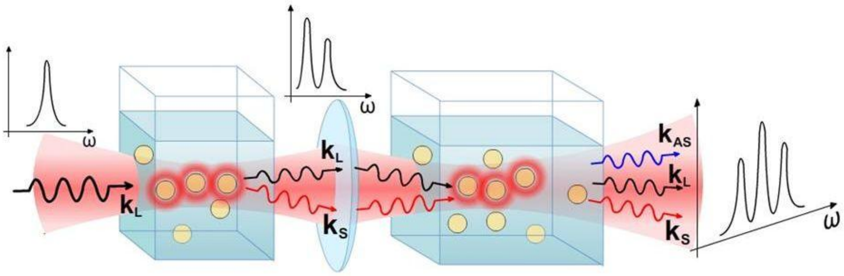

Fig. 1 The scheme of the experiment.

Two cells experimental set up was used. The first cell filled with suspension of submicron particles was used as the source of biharmonic pump. The frequency difference of this two frequency radiation was tuned by using different particles possessing different acoustic eigenfrequencies. At the case of exact coinciding this biharmonic pump frequency shift with the acoustic eigenfrequencies of the submicron particles in the second cell the effective generation of anti-Stokes component of low-frequency Raman scattering takes place. In our work we used suspensions of latex, silver and diamond particles with sizes of 200-400nm.

The reported study was funded by RFBR (projects № 19-02-00750-a and № 19-02-00440-a).

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Webinar presentation

Anisotropic gold nanoparticles conjugates as a prospective tool of tumor cells imaging: study by stimulated surface-enhanced Raman microscopy

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This report is devoted to the synthesis of new plasmonic labels for targeted cancer diagnostics and therapy in the optical range of biological tissues transparency (600-800 nm) supported by their study by stimulated surface-enhanced Raman scattering (SSERS). Stimulated Raman scattering microscopy (SRS) is widely used for label-free biological studies and mapping of tissues. Particularly, SRS methods is applied for the study of distribution and affinity of labels in biological samples [1].

A new type of gold nanoparticles was obtained, having a plasmon resonance peak at 650-750 nm, wherein the developed synthesis gave no particles of other shape as a by-product. Further the nanoparticles were modified with cyanine 5.5 and folic acid, a delivery vector, using the technique of layer-by-layer electrostatic coating (LBL) with polystyrene sulfonate and polydimethyldiallylammonium and using covalent immobilization by amino thiol linkers (Fig 1 a). HeLa cells were chosen as a folate-positive line, and HEK Null cells were tested as a folate-negative line [2].

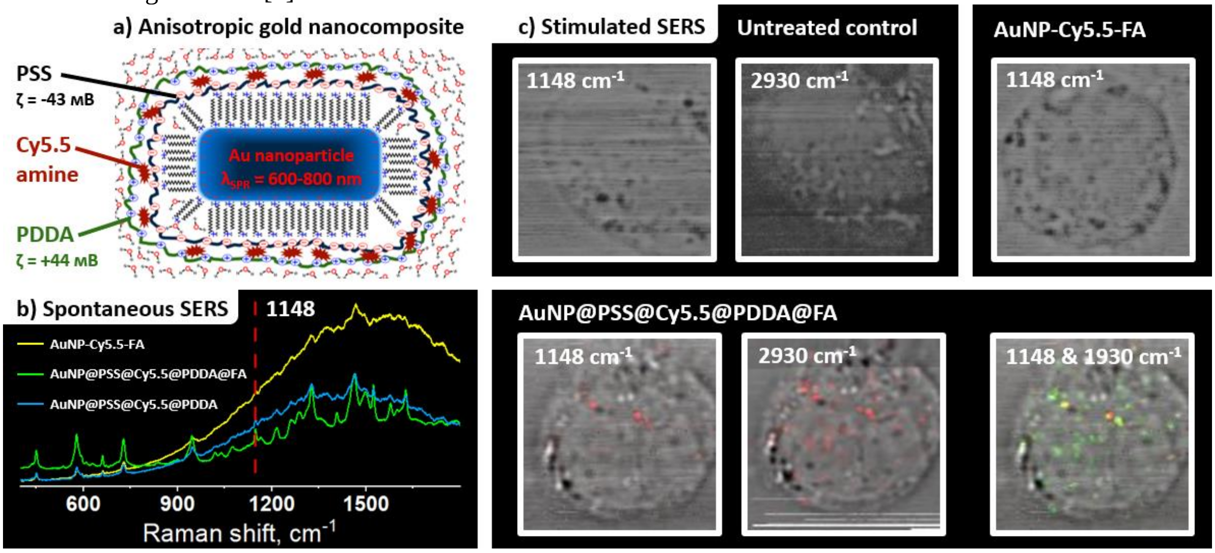

Fig. 1 a) Schematic representation of labels under study b) The SERS spectra of systems selected for mapping by the SSERS. c) Mapping of gold NPs in HeLa cells by the stimulated SERS microscopy, 2h incubation, 3 μg/ml DMEM

We have chosen several most pronounced Raman modes according to the results of spontaneous surface-enhanced Raman spectroscopy studies of nanoparticles in colloidal solutions, which are not overlap with a signal from organic compounds of cells (Fig. 1 b). For the SSERS studies we used Stokes pulse fixed at 1064.1 nm and the pump pulse tuneable according to desired Raman shift (Fig 1 c). At these wavelengths, a control sample (untreated HeLa cells) did not show any scattering (Fig 1 c). Stimulated Raman signal from cell protein (2930 cm^{-1}) located at the same place as Raman signal from nanoparticles (1148 cm^{-1}) proved the presence of LBL-coated nanoparticles by its ability to enhance Raman signal of surrounding biomolecules [3].

Distinctive features of the proposed approach are signal intensity, minimization of interfering contribution to the signal from tissues, biocompatibility, and the use of metal nanoparticles, which is promising for photothermal therapy along with diagnostics.

The research was carried out using equipment of "Research Center for Optical and Laser Materials Research", "Center for Chemical Analysis and Materials Research", "Nanotechnology" and with the support of the German-Russian Interdisciplinary Science Center (G-RISC) funded by the German Federal Foreign Office via the German Academic Exchange Service (DAAD) (Funding Decision on Proposal: A-2021 a-2 r).

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Wednesday September 29th 2021

Session 1

CARS

Invited Speaker

Dr. Rosa Santagata

ONERA, The French Aerospace Lab

Ultrafast ro-vibrational fs/ps-CARS thermometry for combustion: from laboratory flames to a realistic aeronautical combustor

Rosa Santagata is a research scientist working at ONERA, the French national aerospace research center, in Palaiseau (France). After the bachelor and master studies at the University of Naples 'Federico II' (Italy), she obtained her doctoral degree in Experimental Physics in 2015 from the University of Siena (Italy), working on the realization and characterization of an ultra-stable ring laser gyroscope for the detection of general relativity effects. In 2016 she moved to France to start a two years postdoctoral position at Laboratory of Laser Physics (Université Paris 13 – CNRS), where inside the 'Metrology, Molecules and Fundamental Tests' team she worked on the stabilization and frequency tunability of femtosecond and quantum cascade lasers for high resolution molecular spectroscopic measurements in the mid-infrared. Right after she joined as postdoc the 'Laser Sources & Metrology' research unit of the Physics Instrumentation Environment Space Department at ONERA, where at the end of 2018 she was appointed as a permanent research scientist. Her research focuses on fs/ps CARS for high-speed thermometry in high temperature and high pressure media, local or remote gas detection systems (LIDAR) and frequency comb spectroscopy.

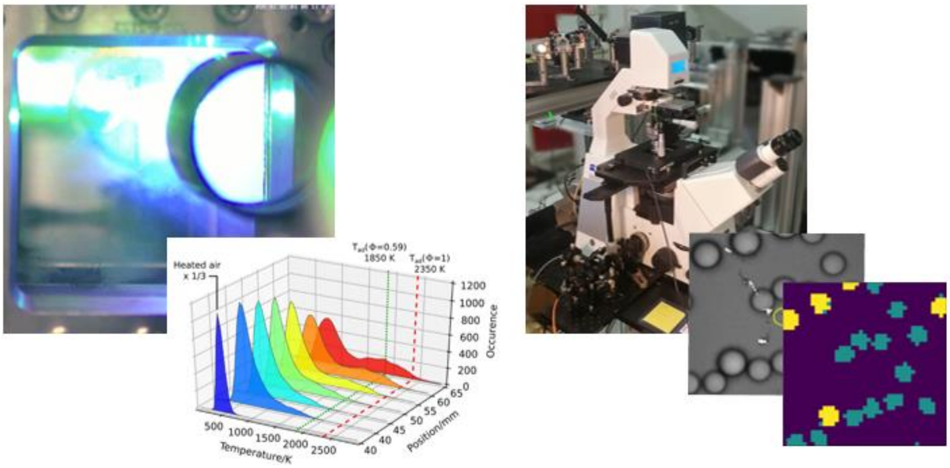
fs/ps-CARS spectroscopy platform for combustion thermometry and hyperspectral microscopy.

Elodie Lin, Michael Scherman, Rosa Santagata, Joanna Barros, Brigitte Tretout, Alexandre Bresson

DPHY, ONERA, Université Paris Saclay, Palaiseau, France

Coherent anti-Stokes Raman scattering (CARS) [1] is widely used to retrieve precise and local information (such as composition, concentration, temperature, pressure) in reactive flows [2]. It is applied in a large range of fields going from combustion and plasma studies to microscopy [3] in condensed media for life sciences and nanomaterials. In particular, hybrid fs/ps-CARS spectroscopy [4] has brought new improvements and has been successfully applied both in gaseous and condensed media providing point information of temperature or chemical composition at high repetition rate (kHz) [5].

Specific laser benches have been developed to match either the high energy and low repetition rate (kHz) requirements of gas phase diagnostics, or the low energy and high repetition rate (MHz) needed for non-destructive characterization of condensed phase microscopic samples. We have developed a compact laser architecture, involving a single femtosecond laser with moderate output pulse energy (1 mJ) and an amplified narrow probe [6] that appears well suited for the two types of applications. The system has been used to perform single shot temperature measurements at kHz rate in laboratory flames with state-of-the-art precision in the range 300-3000 K [7] and in large scale facilities such as representative aeronautical combustors [8]. The laser bench has also been coupled to a microscope in order to perform hyperspectral imaging. First experiments in liquid (toluene) and solid micrometric beads (PMMA and Polystyrene) demonstrate promising performances for characterization and detection of species. Furthermore, the dual architecture allows implementing similar optimization strategies for the two experimental configurations, for instance to reject the background (probe delay, polarization) or to increase the measurement dimension (multi-focus). This demonstrates the potential of this laser architecture for the development of a compact and flexible platform well adapted to a wide range of media and diagnostics.



(a) **(b)**

Fig. 1. (a) Evolution of the temperature distribution in an aeronautic combustor with spatial coordinate in the direction of the flow. (b) Hyperspectral imaging of PMMA and polystyrene beads in water using CARS microscopy.

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Ultrabroadband fs/ps coherent Raman spectroscopy behind optical windows via *in-situ* fs laser-induced filamentation

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Hybrid femtosecond/picosecond (fs/ps) coherent Raman spectroscopy (CRS) is a powerful non-linear optical diagnostic technique, which represents the state of the art in gas-phase thermometry and species concentration measurements. This technique relies on broadband, fs-duration laser pulses to excite the Raman-active modes, and relatively narrowband ps-duration probe pulses to scatter off the coherently excited molecules. The resulting CRS signal is thus generated on a ps timescale, faster than the typical timescale of successive molecular collisions, allowing for simultaneous frequency- and time-resolved spectroscopy. Two-beam fs/ps CRS employs a single fs combined pump/Stokes pulse to induce pure-rotational and vibrational transitions, as constructive pump/Stokes photon-pairs are found across the entire instantaneous bandwidth of the broadband laser pulse. The spectral interrogation window is thus limited by the bandwidth of the pump/Stokes pulse: to excite ro-vibrational modes in the vibrational fingerprint region (~500-1800 cm^{-1}), ultrabroadband transform-limited (TL) pulses with duration of <25 fs are required. The use of ultrabroadband CRS for combustion diagnostics in e.g. enclosed flames, however, is limited by the presence of optical windows, which severely chirp the ultrabroadband pulse, ultimately limiting the instantaneous excitation bandwidth at the measurement location. In the present work we demonstrate the use of fs laser-induced filamentation to generate a compressed supercontinuum behind a relatively thick optical window (~22 mm), and to perform ultrabroadband CRS thermometry.

The experimental setup employs a single regenerative amplifier laser system (Astrella, Coherent), providing ~35 fs TL pulses (~7.5 mJ/pulse, 800 nm) at 1 kHz repetition rate, whose output is split in a pump/Stokes pulse (~2.5 mJ pulse) and in a narrowband ~6 ps probe pulse (~300 µJ/pulse, 400 nm), generated by second-harmonic bandwidth compression (Light Conversion). Spherical lenses (f:=500 mm and 300 mm, respectively) are employed to focus the pump/Stokes and probe beams at the measurement location. The high irradiance of the pump/Stokes beam results in its self-focusing, leading to the generation of a plasma filament: as the pulse propagates in the filament, it experiences self-phase modulation and non-linear dispersion due to the plasma medium, resulting in its temporal compression. We use fs laser-induced filamentation to generate a compressed supercontinuum, with an estimated duration of ~24 fs, *in-situ* at the measurement location, behind a ~22 mm thick BK7 glass window: an external compressor unit is employed to pre-chirp the input pulses and optimize the filamentation process. The resulting ultrabroadband pump/Stokes beam is crossed by the probe beam ~4 mm after the filament, so that no ionization is present in the probe volume and the non-intrusiveness of the technique is maintained. We demonstrate the use of this technique to perform vibrational CRS thermometry in the hot flue gases of a laminar premixed CH_4/air flame. The compressed supercontinuum has sufficient bandwidth to excite the ro-vibrational Raman modes of CO_2 (at ~1200-1400 cm^{-1}) and O_2 (at ~1556 cm^{-1}) and the corresponding ro-vibrational Raman spectra are successfully detected on the basis of a single laser shot.

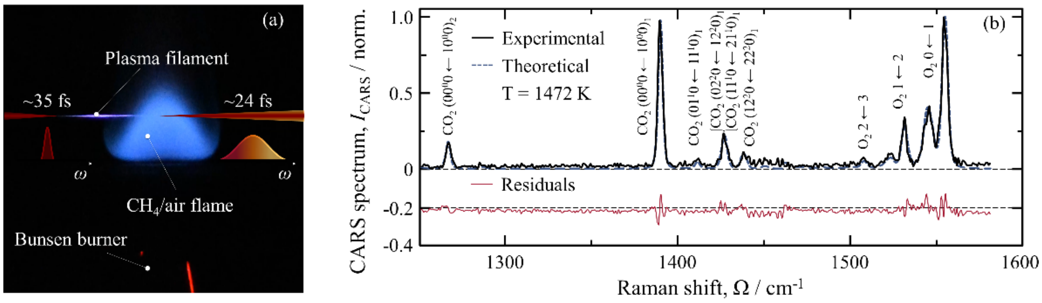

Fig. 1 (a) Plasma filament generated *in-situ*, behind a ~22 mm thick optical window, in a laminar premixed CH_4/air flame. (b) Single-shot recording of the ro-vibrational O_2-CO_2 CRS spectra in the hot flue gases of the flame.

Acknowledgement
We greatly acknowledge the funding provided by the Netherlands Organisation for Scientific Research (NWO), obtained through a VIDI grant (15690) in the Applied and Engineering Sciences domain.

A Study on Carbon Gasification Dynamics using Ultrabroadband Coherent Anti-Stokes Raman Scattering

Yang Ran[1], *André Boden*[1], *Felix Küster*[2], *Stefan Guhl*[2], *Andreas Richter*[2],
Stefan Nolte[1,3], *Roland Ackermann*[1]
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Gasification is an important technology to reduce carbon dioxide emission, as it may convert carbonaceous feedstocks to fuels, chemicals and other products. Thus, a better understanding of the involved processes is highly desirable. Gasification usually occurs at high pressures and temperatures, making experimental investigations challenging. One of the few established methods is the thermal gravimetric analysis (TGA), which measures the weight of the gasified probe [1]. A promising *in-situ* approach is based on femtosecond coherent anti-Stokes Raman scattering (fs-CARS), as the fs-pulse duration makes the CARS signal independent from molecular collisions [2]. In particular, ultrabroadband fs/ps-CARS allows determining the temperature and multi-species concentration from the same spectrum [3, 4]. The essential chemical reaction during carbon gasification is the Boudouard reaction: $C+CO_2 \rightleftarrows 2CO$, $\Delta H = 172$ kJ/mol. With respect to the chemical equilibrium and the reaction kinetics, the highly endothermic reaction shifts to CO formation at temperatures above ~1000 K [5, 6]. In a previous study, we used fs/ps-CARS to determine the temperature from CO_2 CARS spectra (~473-1073 K) [4,7]. Moreover, CO concentrations down to 2% at 1073 K were measured. Based on these studies, we applied fs/ps-CARS to monitor the conversion process. ~400 mg Central German lignite coke powder was filled into a sample holder, installed in the reactor center. The probe region was set above the carbon source in ~1-2 mm distance. A CO_2 atmosphere was controlled at 1.4 bar and the heating rate was 10 K/min. The set temperature of the reactor was controlled with a thermocouple.

Figure 1(a) shows representative CARS spectra from 973 to 1323 K. An increasing CO CARS signal appears above 1000 K. The temperatures determined from 5 CO_2 CARS spectra at ~1-4 ps probe pulse delays are shown in Fig. 1(b) (red points). At reactor temperatures above ~1200 K, the CARS temperature does not follow the reactor temperature, but reaches a plateau. Correspondingly, the CO concentration peaks between ~1200 - 1300 K, indicating the carbon conversion process. For comparison, a CARS measurement without carbon was performed (orange points), where no temperature plateau occurs. Thus, there is clear evidence of a considerable temperature drop of ~200 K, an observation which has not been accessible with previous examination methods. Further systematic CARS studies on carbon conversion are planned in the future.

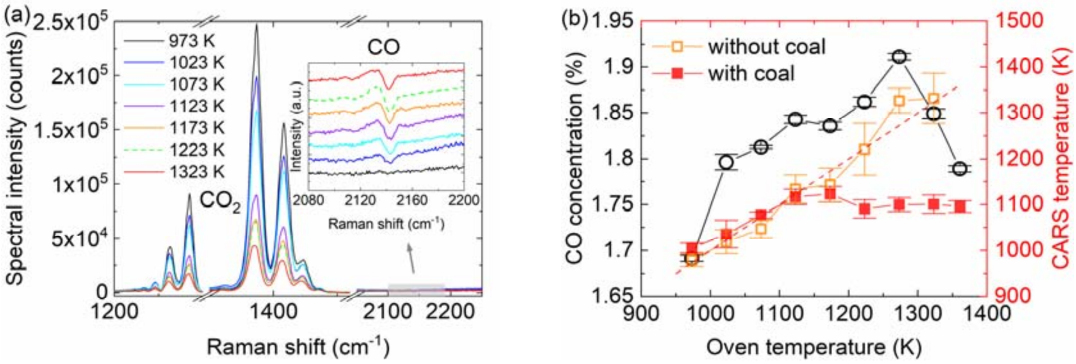

Fig. 1. (a) Ultrabroadband CARS spectra measured at a probe delay of ~1.5 ps during the Boudouard reaction process at 1.4 bar. The legends show the temperatures measured from the thermocouple. (b) Temperature and CO concentration results determined from the CARS spectra. The orange data points show a comparable measurement with empty sample holder.

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Picosecond Optical Parametric Amplifier Pumped by A Thin-disk Laser at 1 µm for Coherent Anti-Stokes Raman Scattering

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Coherent anti-Stokes Raman spectroscopy (CARS) is a powerful tool in combustion diagnostics [1]. The principle of CARS is basically a four-wave mixing process. It needs three beams, the pump, Stokes and probe beam with at least two different wavelengths. For high pressure applications, the use of fs pulses is of additional benefit, as molecular collisions do not distort the CARS signals, if the excited Raman level is probed within a few ps [2]. However, too short pulses (~100-500 fs) result in poor spectral resolution. To investigate the characteristics of each Raman transition of various gases in extremely low concentration, a narrow bandwidth, high power and tunable laser device is needed.

Figure 1 (a) shows the scheme of the developed OPA. The pump source is a thin-disk amplifier (Dira 500-10, TRUMPF Scientific Laser GmbH + CO. KG, Germany) with a maximum pulse energy of 60 mJ and 1 kHz repetition rate. After the long-pass edge filter (LEF), 2.5 mJ of the pulse energy is used to drive the OPA. Inside of the OPA, the second harmonic at 515 nm is used to pump the two OPA stages. The seed spectrum is generated via phase-matched optical parametric generation (OPG) in an OPG/OPA double pass setup. Between the first and second path, the spectrum is significantly narrowed by a folded 4-f shaper with an adjustable slit aperture in the Fourier plane. The grating of the shaper is rotatable to enable a wide tunability of the transmitted centre wavelength. After the double path OPG/OPA-stage, the seed pulse energies have reached µJ levels and are amplified to above 100-µJ in the main OPA stage. The signal output spectrum of the OPA is tuneable over a wide range from 700 to 950 nm with a stable spectral bandwidth of 17 cm^{-1} to 20 cm^{-1}.

In a proof-of-principle experiment, the signal beam of the OPA was used as pump, the fundamental wavelength at 1030 nm as Stokes and the second harmonic (515 nm) as probe to investigate the CARS signals in air. Therefore, we tuned the OPA wavelength to 831 nm and adjusted the probe delay to ~1.6 ps to detect the CARS signal of N_2, at a Raman shift of $\Delta\upsilon$~2330 cm^{-1} ($\upsilon'=1\rightarrow\upsilon''=0$) with a width of 16 cm^{-1} (FWHM), as shown in Fig. 1 (b). This width is sufficient to resolve different vibrational levels of N_2 (e.g. $\Delta\upsilon$~2300 cm^{-1} for $\upsilon'=2\rightarrow\upsilon''=1$), which allows for vibrational ps-CARS thermometry. Further experiments will especially focus on CO_2, for which vibrational levels can be probed with ps-pulses for thermometry at room temperature already [3].

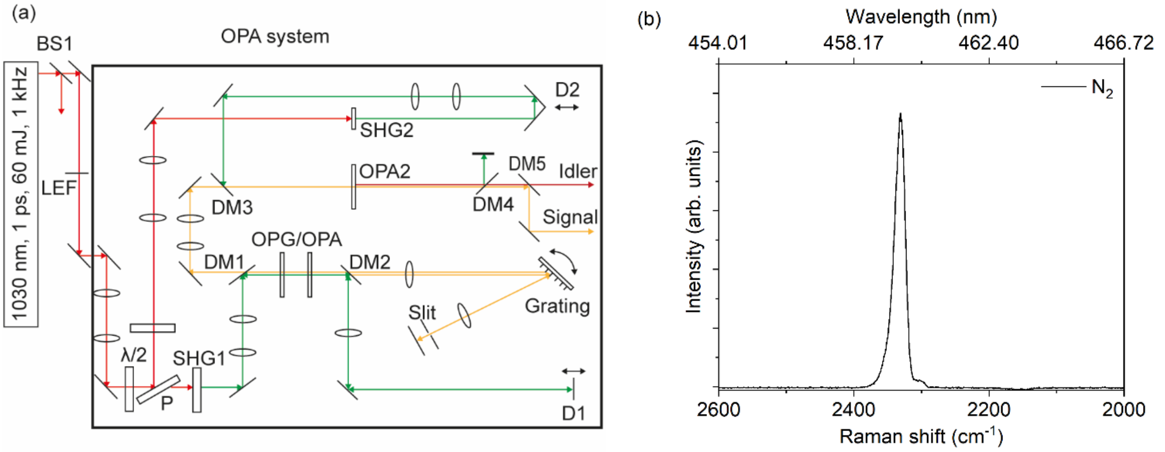

Fig. 1 (a) Scheme of the OPA setup. BS1: Beam splitter with R:T = 50:50. LEF: ultra-steep long-pass edge filter. λ/2: half-wave plate. P: polarizing beam splitter. SHG1-2: BBO nonlinear crystals. D1-2: motorized delay stage. DM1-5: dichroic mirrors. (b) The vibrational Raman spectrum of N_2 in air. The probe delay time is set at 1.6 ps to avoid nonresonant signal.

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Wednesday September 29th 2021

Session 2

χ^2 Spectroscopy 3

Invited Speaker

Prof. Dr. Björn Braunschweig

Westfälische Wilhelms-University Münster
Institute of Physical Chemistry and Center for Soft Nanoscience

Remote Control of Photoswitchable Amphiphiles at Aqueous Interfaces

Björn Braunschweig is a professor at the Institute of Physical Chemistry of the Westfälische Wilhelms University Münster since 2017. After studying physics and receiving the doctoral degree at TU Clausthal in 2009, he moved to the University of Illinois at Urbana-Champaign for a postdoctoral stay with Feodor Lynen fellowship and moved 2011 to the Friedrich-Alexander University Erlangen-Nürnberg, where we was a group leader at the Institute of Particle Technology (LFG) until 2016.

Research interests are in electrocatalysis and soft matter interfaces where surface specific nonlinear optical spectroscopies such as sum-frequency generation (SFG) and second-harmonic scattering (SHS) are applied for molecular level characterization. In addition, new methods for characterization of ultrathin films with vibrational spectroscopy are being developed, while also orthogonal methods to SFG spectroscopy like surface tensiometry and surface dilatational rheology help to address adsorption, ion specific effects and interactions at interfaces on a molecular level. Relatively new research topics are on responsive interfaces and active soft matter systems that can react to light and temperature stimuli.

Remote Control of Photoswitchable Amphiphiles at Aqueous Interfaces

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An ongoing endeavour in chemistry is to structure hierarchical materials with novel properties that are inherited by their molecular building blocks and to implement (re)active elements. The use of functional building blocks, which are responsive to light, allows us to assemble and to manipulate superstructures at interfaces with new properties. For that, precise and remote control of chemical reactions in both time and space is required to drive a system from one equilibrium state to another. This can be achieved by photo-responsive molecules at interfaces as well as in larger hierarchical elements of materials.

We report on E/Z photo-isomerization of new photo-switchable arylazopyrazole (AAP) surfactants [1,2] at aqueous interfaces. AAP derivatives are a new class of photoswitches that exhibit photostationary states and thermal lifetimes superior to most azo derivatives. At interfaces AAP amphiphiles can drastically and reversibly change their surface activity when there are switched from the E to the Z form with green (E) or UV (Z) light irradiation. Using IR-Vis vibrational sum-frequency generation (SFG) we address the molecular structure changes at the interface and complement SFG spectroscopy with surface tensiometry and neutron reflectometry. E/Z photo-isomerization of AAP surfactants at the air-water interface causes large and reversible changes in surface tension and surface coverage Γ. We show that a strong non-resonant contribution to the second-order electric susceptibility from interfacial AAP surfactants exists and heterodynes CH and OH contributions to the SFG spectra. Although this complicates the SFG spectra and causes highly dispersive line shapes, the non-resonant contribution is also helpful to trace the surfactants' surface excess. This is demonstrated by a comparison of SFG spectroscopy with neutron reflection. Further, the interference with the broad OH bands from interfacial water molecules can be used to determine the net orientation of water at the interface. While the charging state of ionic surfactants at interfaces is intuitively clear, it is important to determine the interfacial charging for polymer/surfactant mixtures. Indeed we can demonstrate that at air-water interfaces covered with complexes of polystyrene sulfonate and AAP surfactants, water molecules in the first molecular layer at the interface change their net orientation when the AAP surfactants are switched in their conformation. This "flip flop" in orientation is directly evidenced by SFG spectra and associated to apparent charge reversal at the interface. For this analysis we make use of a third-order contribution to the nonlinear electric susceptibility that arises from the interfacial electric double layer and is useful to trace double layer potentials [3].

We have also applied SFG to resolve structure changes and to probe the existence of structures with local inversion symmetry. We show that butyl-AAP sulfonates [1] undergo a monolayer to bilayer transition that is responsible for unprecedented changes in surface tension and Marangoni flows at extended surfaces but also in thin liquid films and macroscopic foam.

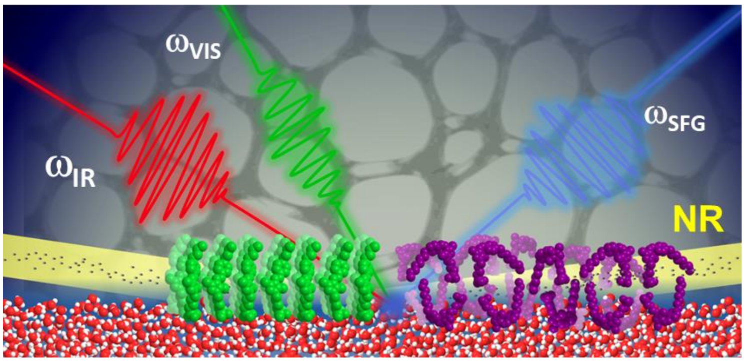

Fig. 1 Schematic diagram of the three photon process of SFG and proposed molecular structures of AAP sulfonates [1] at the air-water interface when there are switched from a SFG active structure (E form, green) to centrosymmetric structure that is SFG inactive (Z form, violet).

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Revisiting the Redox Behavior of Gold Surfaces via Sum Frequency Generation

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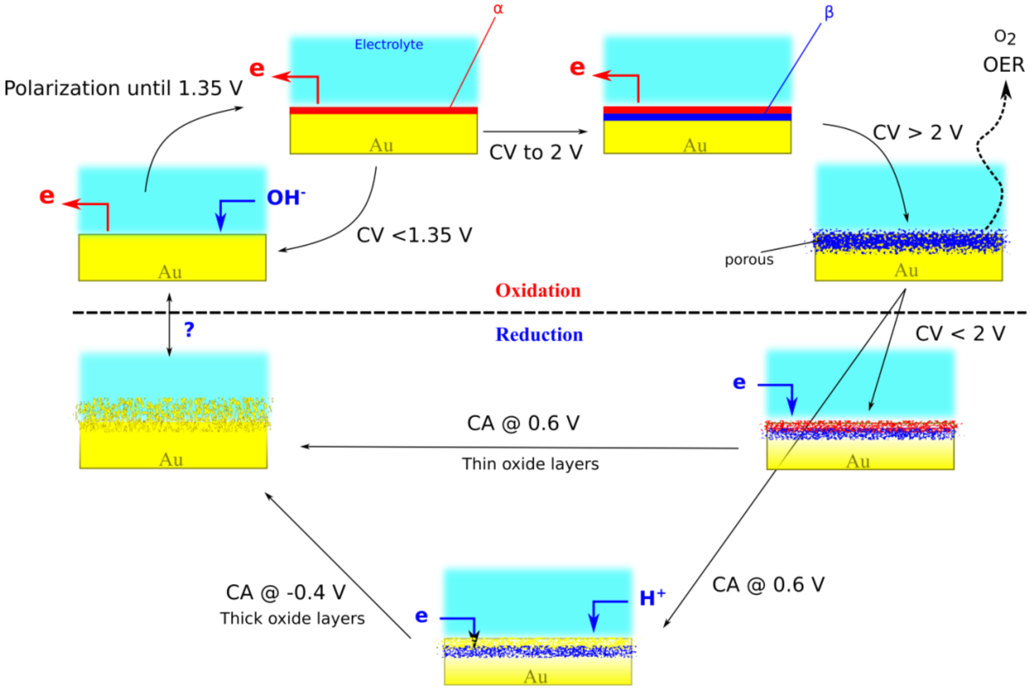
Abstract

We combine herein electrochemistry and sum frequency generation to understand the various steps for the redox reaction of polycrystalline gold in acidic medium. This combination reveals crucial information about mechanistic steps for the formation and reduction of α and β gold oxides. In this presentation, various processes will be discussed such as surface reactions, double layer reactions, and the presence of sub-oxide layers.



Scheme1: Schematic representation for the redox cycle of polycrystalline gold in acidic medium revealed via sum frequency generation.

Amino Acid Based Carbon Quantum Dots for Detection of Heavy Metal Ions Studied by Sum Frequency Generation Spectroscopy

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Carbon quantum dots (CQDs) have been extensively explored in various fields of science after their accidental discovery in 2004 by Xu et al. while purification of single wall carbon nanotubes [1]. In comparison to conventional quantum dots, CQDs have better water solubility, high quantum yield, biocompatibility, high photostability and low toxicity. CQDs are comprehensively being used in the arena of chemical sensing, photocatalysis and bioimaging [2]. Two strategies are being employed for fabrication of CQDs i.e. top down and bottom up. Laser ablation, hydrothermal treatment, arc discharge and microwave are some of the techniques utilized for the synthesis of CQDs. By using conventional spectroscopic tools it is difficult to probe the interfacial activities of the CQDs and their impact on water structure. In this work, we have used a highly surface sensitive and chemically specific sum frequency generation (SFG) spectroscopic tool to probe the CQDs and pristine water interface. Three major peaks are observed in the SFG spectrum of the neat water which is consistent with the literature reports [3]. The sharp peak at 3700 cm^{-1} corresponds to the free –OH (dangling bond) groups present at the interface pointed upwards, another peak 3400 cm^{-1} corresponds to the weakly coordinated hydrogen bonding (liquid-like) water molecules and the peak 3200 cm^{-1} corresponds to strongly hydrogen bonded (ice like) water molecules which has tetrahedral bonding conformation. This type of distribution is obtained due to the asymmetric environment of the water molecules present at the interface. It is found that the presence of the carbon quantum dots strongly affect the water ordering and its hydrogen bonding coordination at the air-water interface. The enhancement in the intensity of peaks at 3200 cm^{-1} and 3400 cm^{-1} clearly depicts CQDs role in changing the ordering of the interfacial water structure. The detailed analysis on the conformational changes of CQDs and the role of interfacial water molecules would be explored.

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Webinar presentation

Posters

September Mon 27th and Tue 28th 2021

Determining the Apparent Charge of E.Coli Membranes using Sum-Frequency Generation Spectroscopy

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Lipids play a central role in many biological systems as they are the main structural component of membranes, which not only separate cells and their organelles from the surrounding environment but also serve as an important platform for reactions. A central characteristic of any membrane is its charge distribution, as this influences not only the properties of the water which it is in contact with, but also the spatial distribution of ions and other solutes in proximity to the membrane. This in turn may affect processes such as ion and metabolite transport across the membrane or even protein folding.

While it is well known that most lipid headgroups are either zwitterionic or negatively charged at physiological pH, it has remained challenging to accurately determine the effective charge of biological membranes, as they are commonly comprised of many different lipid forms and the effective charge of these individual components in vivo is largely unknown.

It has recently been demonstrated that the charge of a lipid layer at low charge density can successfully be determined by means of titration using a lipid of known charge [1]. The lipid in question is deposited onto an aqueous solution and the surface titration is observed via the orientational order that the changing charge of the mixed lipid layer imposes onto the water subphase. Making use of the selection rule of second-order non-linear spectroscopy, namely that it is forbidden in centrosymmetric media, the induced degree of order in the interfacial water region is probed via sum-frequency generation spectroscopy. In other words: A highly (negatively) charged lipid layer may strongly orient the interfacial molecules of the aqueous subphase, yielding a strong OH stretch band in the sum-frequency-generation spectrum. As the relative fraction of (positively) charged lipid is increased in the system the net charge of the lipid layer will reduce and less orientational order is imposed on the water structure, which in turn is observable as a decreasing OH stretch band area until the point of zero charge is reached. This point of zero charge could be used to deduce the apparent charge of the unknown lipid.

Here, we apply this technique to determine the apparent charge of a highly complex lipid layer, namely the one found in the membrane of the E.coli bacterium, which is mainly composed of zwitterionic as well as singly and doubly negatively charged lipids. Our results further illustrate the use of this technique in characterising the biophysical properties of soft interfaces that have so far been challenging to ascertain.

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Unexpected behavior of sodium sulfate observed in experimental freezing and corrosion studies

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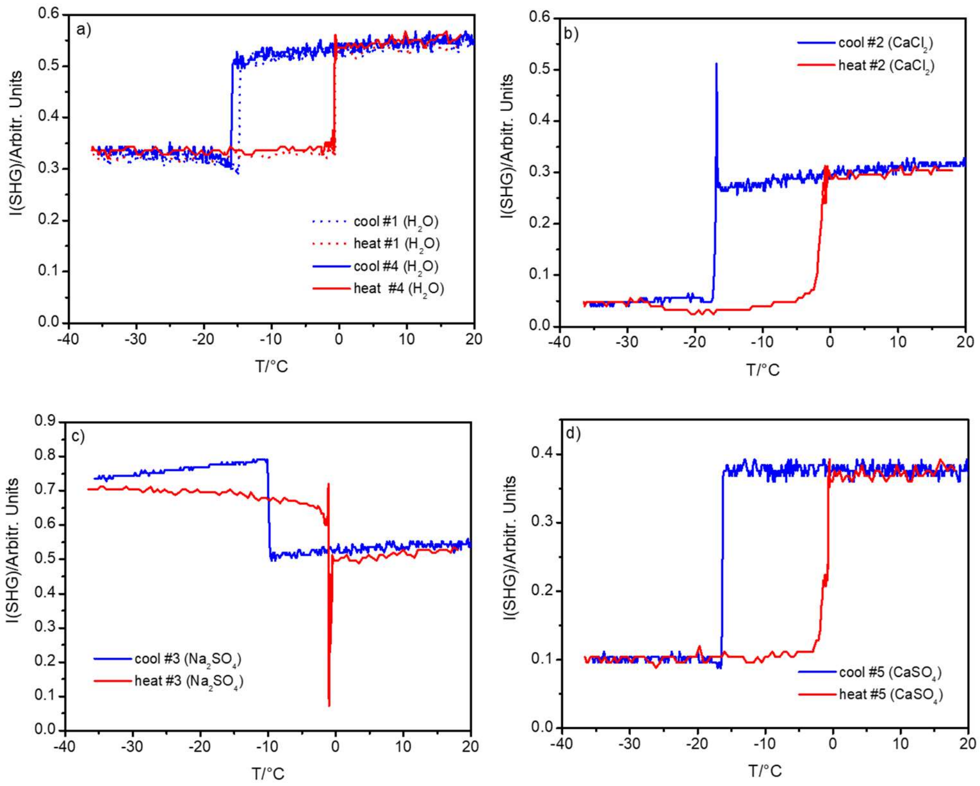
We report two distinct studies that shown unexpected behavior with respect to sodium sulfate in contact with flat surfaces. On the one hand, we investigated immersion freezing of sulfate containing solutions ($CaSO_4$ and Na_2SO_4) in the presence of flat sapphire-0001 crystals using second harmonic generation (SHG) spectroscopy. Control experiments were carried out with neat water and $CaCl_2$. The SHG signals from $CaSO_4$ and Na_2SO_4 solutions behave somewhat differently from those sensed in both cases, the neat water and $CaCl_2$. The common pattern shows a decrease of the SHG signal with decreasing temperature until about -15 °C, whereupon the signal sharply drops, indicating freezing. With the Na_2SO_4 solution, although the signal initially follows closely the neat water curve, the trend increases sharply at about -10 °C followed by a gradual decrease with further cooling. There is no plausible explanation for the distinct behavior of the Na_2SO_4 solution and thermodynamic calculations do not suggest any precipitation of a sodium sulfate solid phase. At the end of the freeze-thaw cycle the initial SHG for each system is retrieved, suggesting reversibility. On the other hand, in a separate non-freezing study, it was observed that sodium sulfate precipitates form solution on flat steel surfaces at room temperature although, as in the freezing experiments, thermodynamic calculations do not indicate that precipitates should be forming. The form of the crystals observed on the steel samples has snowflake shapes similar to one literature report. We conclude that Na_2SO_4 in the presence of flat surfaces shows unexpected behavior that should incite further detailed studies in future work to elucidate the phenomenon.



Freeze-thaw cycles for water (a) and 15 mM solutions of CaCl2 (b), Na2SO4 (c) and CaSO4 (d)

Immersion versus Deposition Freezing on the Sapphire (1120) Surface: a Sum-Frequency Generation Study

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Mineral aerosol particles show a large variability in ice nucleation ability in the atmosphere. Much insight has been gained on water freezing as a function of mineral surface properties, water pH and salinity, and supersaturation conditions. Although it is clear that different freezing pathways show different onset conditions[1], these differences remain poorly understood, particularly on the molecular level. Our previous work showed that surface charge and surface aging in aqueous environments play significant roles in influencing the rearrangement of water molecules at the surface of a mineral during cooling and freezing, hence affecting the ice nucleation ability of that surface[2-4]. Here, we use an environmental cell in conjunction with nonlinear spectroscopy, mainly sum-frequency generation (SFG) to address molecular-level differences between two common freezing pathways, immersion freezing (IF) and deposition freezing (DF), in the atmosphere on a mineral surface that is free of free-dangling-OH groups (1120-cut Al_2O_3). We find that DF leads to a highly coordinated water structure compared to IF. In the case of DF, SFG signals depend on whether the supersaturation condition has been approached via temperature change or RH change. The presentation will focus on the spectroscopic discrimination between immersion and deposition freezing and discuss recent findings, including the effect of temperature and humidity on the ice structure.

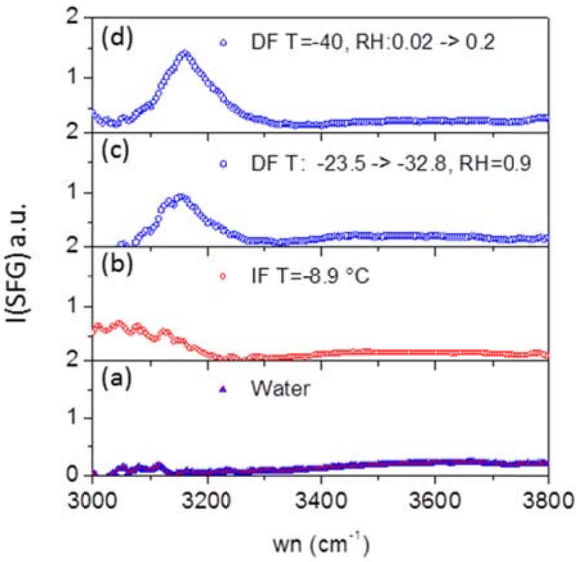

Fig. 1 SFG at the water- and ice-Al_2O_3 1120 interface: (a) water at 20°C, (b) ice after immersion freezing at -8.9 °C, (c) ice after deposition freezing at constant RH, and (d) ice after deposition freezing at constant temperature.

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Cascaded coherent anti-Stokes Raman scattering for high-sensitivity number density determination in the gas phase

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Hybrid fs/ps coherent anti-Stokes Raman scattering (CARS) is a powerful type of CARS spectroscopy taking advantage of picosecond probe pulse duration eliminating the nonresonant four-wave mixing contribution and collisional dephasing of a wavepacket. Recently, hybrid fs/ps CARS has been succesfully demonstrated for gas-phase thermometry with <2-3% inaccuracy and precision and relative species concentration measurements. This high trueness level of temperature measurements allows one to perform accurate reacting flow characterization and improve the efficiency of modern combustors. On the other hand, high-accuracy concentration measurements are required for chemical rate analysis in gases. It is well known that the CARS signal scales quadratically with number density of scattering particles providing great level of sensitivity sufficient in may applications. In this work, we are going to explore a higher-order non-linear process known as cascaded CARS (CCARS). In this process, coherent Raman scattering occurs twice: (i) the probe field scatters from the Raman coherence producing a CARS field, (ii) the CARS field scatters from the Raman coherence again and producing a CCARS field. We are exploring the CCARS signal power scaling and number density scaling.

The experimental setup was implemented based on the two-beam femtosecond/picosecond phase-matching scheme, achieved by means of a single regenerative amplifier laser system. The laser pulses originate from the ~35 fs output of a high-power femtosecond regenerative amplifier, with a pulse energy of ~7.5 mJ provided at a 1 kHz repetition-rate (Astrella, Coherent). A narrowband ~6 ps-duration full-width-at-half-maximum (FWHM) probe-beam, centred at 400nm, is efficiently produced according to the principle of second-harmonic bandwidth compression (Light Conversion). The pump/Stokes and probe beams are intersected collinearly in the mixture of N_2 and Ar at ambient conditions. The single-shot CARS and CCARS spectra were acquired at 1000 Hz frame rate with a sCMOS camera (Zyla, Andor).

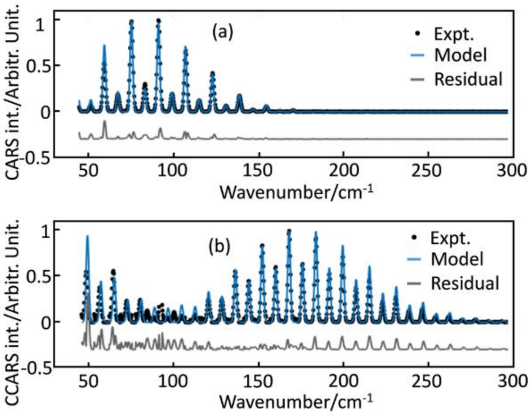

Fig. 1 Single-shot CARS (a) and CCARS (b) experimental spectra acquired from 80% N_2 and 20% Ar mixture and corresponding fitting curves.

In this work we demonstrate simultaneous detection of CARS and CCARS spectra using a two-channel spectrometer employing polarization separation of both signals. We explore the sensitivity of CCARS signal to the number density of scattering molecules in the gas mixture, and to the power scaling of the pump/Stokes and probe input laser pulses.

Acknowledgement

We greatly acknowledge the funding provided by the Netherlands Organisation for Scientific Research (NWO), obtained through a VIDI grant (15690) in the Applied and Engineering Sciences domain.

Simultaneous multifocus CARS spectroscopy for gases and microscopy

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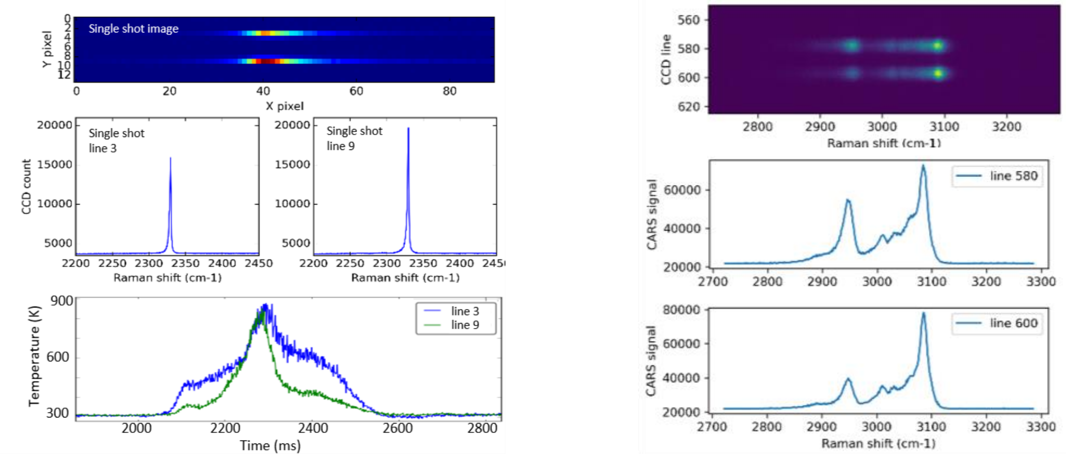
Coherent anti-Stokes Raman scattering (CARS) spectroscopy is known to be very powerful for the study of reactive flows [1] and can also be applied to microscopic sample [2]. Hybrid fs/ps regime [3] has brought new improvements and has been successfully applied both in gaseous and condensed phase media providing point information of temperature or chemical composition at high repetition rate (kHz). To increase the field of application of the technique to non-stationary media, 1D [4] and 2D [5] schemes were implemented to retrieve hyperspectral data in single-shot. Nevertheless, both schemes require very high level of energy per laser pulse to generate an efficient CARS process. When working with moderate energy levels, we propose here to increase the amount of spatial information obtained in single shot at lower energy cost. By using multiple laser spots, multi-point spectral information can be recorded. Multi-focus setup has already been implemented [6] but was used to increase the speed of CARS imaging performed at a precise wavenumber.

In this study, a single set of laser beams, designed for hybrid fs/ps-CARS [7] is split into two focal spots using a home-made beam divider. Two anti-stokes beams are thus generated and imaged on the entrance slit of the detection spectrometer, allowing simultaneous 2-point-CARS spectroscopy. 2-point single shot spectroscopy of N_2 Q branch is demonstrated in heated air and in BOXCARS geometry with 3 mm distance between the two points (Fig. 1(a)). The setup has been running at 1 kHz during 10 seconds duration to perform temperature measurements when the flame is moved near the measurement volumes (bottom curve). A similar scheme has been applied to a collinear beams geometry, demonstrating 2-point-CARS spectroscopy of toluene in a microscope with 38 µm separation between the two points.

These demonstrations further prove the potential of intermediate laser power CARS systems by providing more spatial information at minimum cost in energy and with increased spatial resolution. Gradients knowledge and multiple points probing may indeed be of great interest for turbulent media diagnostics. In CARS microscopy, it is an efficient way to increase acquisition rate in hyperspectral imaging or to simultaneously acquire a signal of interest while being able to compare it to a reference sample. To go further, this scheme may be easily adapted to generate multiple points arranged in line or in array-like shapes.



(a)

(b)

Fig 1 (a) Single shot CARS spectroscopy of two measurement points spaced by 3 mm : (up) CARS image, (middle) single shot N_2 CARS spectra, (bottom) 1 kHz thermometry in heated air near a flame. (b) Simultaneous CARS spectroscopy of two points spaced by 38 µm in liquid toluene retrieved in a hyperspectral CARS microscope: (up) CARS image, (middle/bottom) simultaneously recorded CARS spectra.

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Oxygen S-branch Raman linewidth determination in O_2-N_2 mixtures

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The Raman linewidth is a crucial parameter for the evaluation of coherent anti-Stokes Raman scattering (CARS) spectra with respect to thermodynamic properties like temperature and concentration [1]. Therefore the determination of rotational Raman linewidths of different molecules and mixtures under various thermodynamic conditions is an important task in modern development of pure rotational CARS [2–7]. Oxygen and its mixtures are of special interest because the development of combustion processes towards oxy-fuel combustion, where the well established N_2-RCARS thermometry cannot be used, necessitates suitable measurements techniques.

Determination of oxygen S-branch Raman linewidths from the coherence decay requires consideration of ^{S}S-branch coherence beating, resulting from spin-rotation coupling [7–10]. Figure 1 shows a simulated coherence decay curve calculated with the model function for the oxygen coherence decay from [7] using the same delay steps as our CARS-experiments and adding noise (black stars). Obtaining the correct linewidth from the fit relies strongly on the correct representation of the cusp in the curve as can be seen from the unaltered coherent fit curve (red). The function fails to represent the late decay properly, resulting in a deviation from the preset linewidths used in the simulation of 10.7%. This is due to a strong weighting of the early decay compared to the late decay, due to the exponential nature of the dephasing. This behavior occurs predominantly for short decay times and small signal intensities, typical for low oxygen concentration mixtures at elevated temperatures. Two methods to overcome this challenge were tested. The first method was a linearization of data and function by taking the logarithm. The second method retains the function, but weights the data points. In figure 1 both modifications succeed in modeling the late decay. This work contains a statistical comparison of both models and discusses their impact on the evaluated linewidth of pure oxygen and oxygen containing gas mixtures at different temperatures.

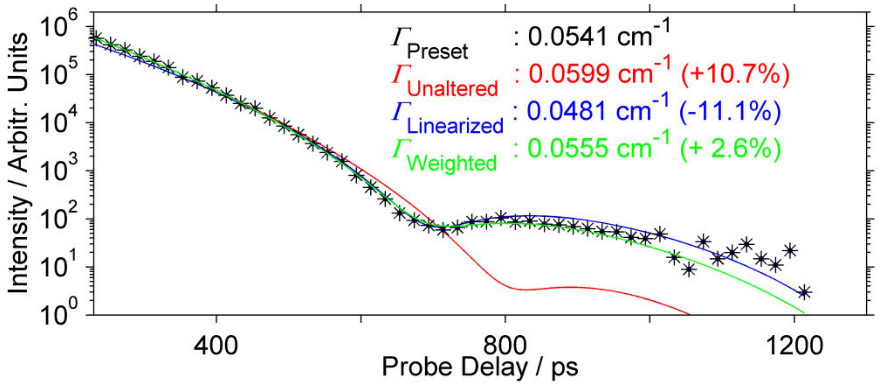

Fig. 1 Simulated coherence decay (black stars) of the *N*'' = 33 line of pure oxygen using a linewidth (proportional to the inverse of the decay constant) of 0.0541 cm^{-1} (black stars). Lines represent best fits of the unaltered coherence dephasing model from [7] (red), the linearized model (blue) and the unaltered model using weighted data (green). Numbers show the resulting linewidths from the fit with relative deviation from preset linewidth.

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Broadband Coherent Anti-Stokes Raman Spectroscopy as a Platform for Rapid Label-free Cytology

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The Biophotonics research laboratory at Maynooth University is engaged in multidisciplinary research focused on label-fee classification of different cell types. To date we have applied Raman micro-spectroscopy in conjunction with multivariate statistical classification algorithms in order to differentiate cells. An overarching goal is the non-invasive diagnosis of bladder cancer and cervical pre-cancer (Pap Smear) based on the use clinically relevant cell sample preparation technique; in particular, we use the ThinPrep standard for cell fixation and slide deposition. With a view to faster sample processing times our group is currently developing a coherent spectroscopy platform that will build on our existing expertise in cytology. Here, we describe a new project that has recently begun in the Biophotonics laboratory in Maynooth University which uses broadband CARS (Fig. 1). Coherent anti-Stokes Raman spectroscopy (CARS) is a rapid, label-free technique for identification of chemical species via chemically relevant molecular vibrations.

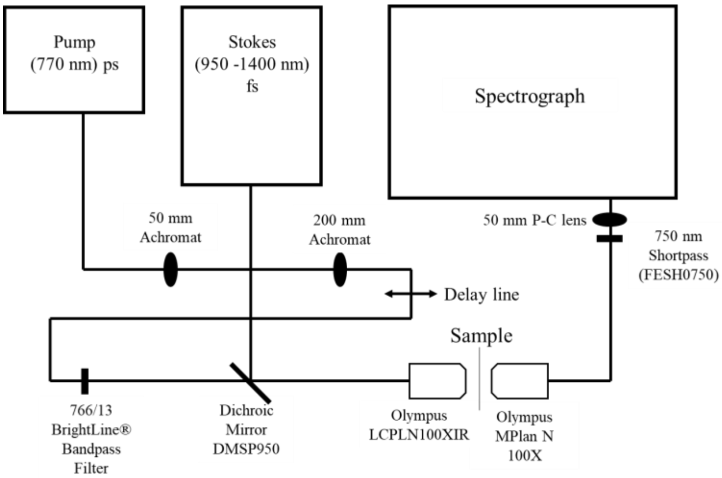

Fig. 1 Schematic diagram of BCARS system. The system uses a custom-built microscope stage with an Andor Shamrock spectrograph.

The detection and quantification of cellular material and of other chemical/biological species in a cytological platform is key to the development of widely applicable, fast and accurate diagnosis based on liquid biopsy. This work aims to develop a microfluidic CARS platform with broadband CARS functionality, based on the platform originally developed by Cicerone et al [1]. The system is optimised for fingerprint region spectra (600 – 1700 cm^{-1}) through shaping of the Stokes beam; generated via three-colour CARS generation. We briefly present a review the state-of the art of Raman cytology, as well as broadband CARS. In addition, we present a plan for the adoption of this platform for clinical pathology.

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Deep Convolutional Neural Network for Non-Resonant Background Removal in Broadband Coherent Anti-Stokes Raman Spectroscopy

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Broadband Coherent Anti-Stokes Raman Scattering (B-CARS) enables Raman spectra in the whole biologically relevant frequency region (500–3500 cm^{-1}). B-CARS could potentially serve as a robust diagnostic platform for a wide range of applications such as label-free flow cytometry but is impeded by the presence of a non-resonant background (NRB) signal. Although numerical approaches exist to account for the NRB, they require an estimate of the NRB in the form of a separate measurement[1], [2]. Similarly, experimental approaches often require complex alterations to the spectroscopy platform, and multiple measurementsRecently, deep learning and neural networks have emerged as a potential solution to account for the NRB. In this work, we propose a deep neural network architecture called VECTOR (Very dEep Convolutional auTOencodeRs), which recreates the analytical Raman-like spectrum from CARS spectra through training of simulated noisy CARS spectra, without the need for an NRB reference measurement [3], [4]. The encoder is trained on simulated spectral datasets, with a range of peak widths and signal complexity, which emulate the different forms of Raman and CARS spectra from different types of samples.

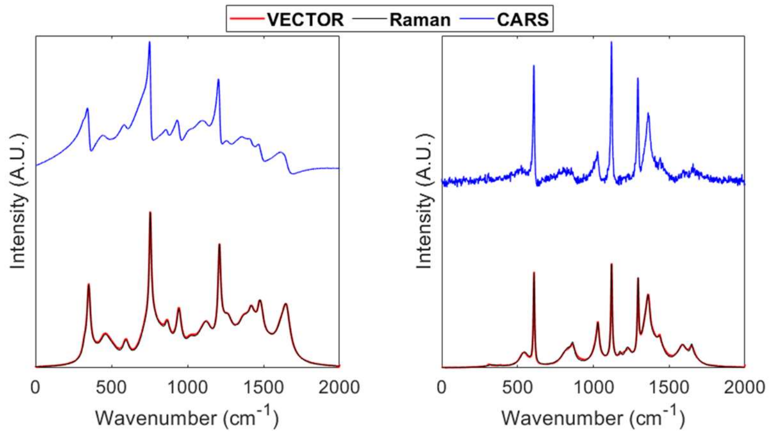

Fig. 1 Example Raman spectrum (red) recovered from input CARS spectrum (blue) from VECTOR network. High (left) and low (right) SNR spectra shown. True Raman spectrum overlaid in black.

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Time-domain pure-rotational N_2 CARS signal dephasing as a method for determining water vapor concentration in hydrogen flames

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Coherent anti-Stokes Raman spectroscopy (CARS) is a powerful laser diagnostic technique to determine scalars in gas-phase combustion applications. Among the advantages of this quantitative measurement technique are the chemical specificity, the capability for high-precision thermometry (~1-3%), and its robust applicability in harsh measurement environments such as flames and plasmas for instance. In addition, time-resolved fs/ps CARS allows for resolving the temporal evolution of the induced Raman coherence provided by short-pulsed laser excitation fields. This evolution is significantly affected by collisional energy transfer between the active and the perturber molecules in the gaseous mixture, resulting in a rotational state-dependent decay of the CARS signal in time (*J*-dependence), which is highly sensitive to changes in temperature, pressure and gaseous mixture composition. In the present work we propose a new technique for measuring the absolute water vapor concentration in flames derived from the *J*-dependent dephasing rate of the pure-rotational N_2 CARS signal affected by inelastic collisions with H_2O. Experiments are performed in a laminar H_2 diffusion flame, where the two main species H_2O and N_2 are present in the products. The pump and Stokes photons, provided by broadband near-transform-limited ~35 femtosecond duration laser pulses, coherently excite pure-rotational N_2 transitions. Thermometry at atmospheric pressure is performed by employing a ~10 ps-duration probe pulse to generate the CARS signal at a short probe delay of 10 ps, when collisions are negligible. The water vapor mole fraction is inferred from a second spectrum recorded at much longer probe delays (~350 ps), when the N_2 CARS signal coherence decay is manifested by binary N_2-N_2 and N_2-H_2O collisions.

Acknowledgement

We greatly acknowledge the funding provided by the Netherlands Organisation for Scientific Research (NWO), obtained through a VIDI grant (15690) in the Applied and Engineering Sciences domain.

Operation of a Fourier-Transform Impulsive Stimulated Raman Spectrometer with Single Femtosecond Oscillator

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Low-frequency Raman spectra (<200 cm^{-1}) are interesting for studies of intra-molecular vibrational modes of large molecules or heavy functional groups, and for studies of inter-molecular force constants. This region can be accessed by spontaneous Raman using triple monochromators, which however represents an expensive and cumbersome solution with relatively low signal yield. More recently, special Bragg filters have been developed to overcome these shortcomings, but they have the disadvantage of being laser excitation-wavelength specific.

A different approach takes advantage of Raman coherence, namely Impulsive Stimulated Raman Scattering (ISRS), allowing excitation of vibrational modes within the bandwidth of ultrashort laser pulses [1], and generation of intense signals due to the coherently prepared vibrational state. In recent papers [2-5], several methods to detect ISRS signals in setups equipped with a single low-energy femtosecond laser were proposed, having different levels of complexity to meet the necessary requirements on high sensitivity, noise rejection and data acquisition speed, and enabling characterization of transparent samples.

In the common practice, spectral or refractive changes, induced in a probe pulse by the Raman coherent field generated in the sample by a preceding pump pulse, are measured as function of the pump-probe delay. The signal at each delay point can be detected using lock-in techniques by chopping the pump beam (delay averaging); alternatively the delay-dependent signal can be obtained by averaging the time-dependent signal produced by a continuous periodic scanning of the delay (scan averaging).

Here, we show that a simple implementation of the scan-averaging scheme allows for measurements of signals from diffusive/slightly absorbing samples which cannot be characterized using the delay-averaging method because of strong thermo-optical, depolarization and beam scattering artifacts. Also, the scan-averaging technique is inherently faster than delay averaging, and enables real-time visualization of the Raman spectrum.

Finally, we compare the ISRS signals obtained by refractive and spectral detection, as shown in Figure 1: while comparisons are available for a Sagnac interferometer [6], we explore the performances of a more common Michelson interferometer to highlight advantages and criticalities of the two detection methods for optimized characterization of samples with different properties.

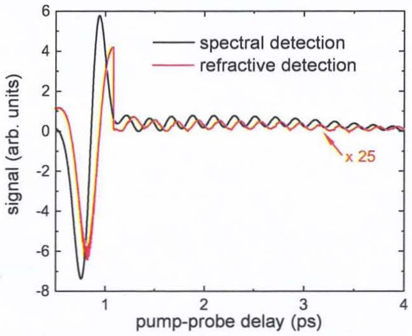

Fig. 1. Comparison of signals from spectral and refractive ISRS detection measured on a CH_2Br_2 sample using a scan-averaging method in a setup using a Michelson interferometer.

This work was performed in the frame of the "Grande Rilevanza" Project US19GR13 co-funded by MAECI.

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Intracavity Stimulated Low-Frequency Raman Scattering

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Stimulated intracavity Raman scattering is widely used not only as a highly sensitive spectral method, but also as a practical way to increase the efficiency of Raman lasers. Effective intracavity stimulated light scattering is realized not only for first Stokes component but also for higher orders Stokes components [1] and this allows to significantly expand the spectral range of the generation of intracavity Raman converters. Stimulated low frequency Raman scattering (SLFRS) [2] which is a result of electromagnetic wave interaction with acoustic eigenfrequencies of submicron particles system provides the possibility to obtain the generation of Stokes and anti-Stokes components with spectral shift determined by the morphology of the active medium. Depending on the characteristics of the system, this spectral shift lies in the gigahertz range (for systems of submicron particles) or the terahertz range (for nanoscale particles). Intracavity SLFRS [3,4] not only gives effective possibility for the acoustic properties of submicron and nanoscaled systems investigation but also is an efficient source of the generation a spectral comb with a difference frequency in the giga- and terahertz ranges. Here we report on the experimental realization of the efficient intracavity SLFRS generation for both disordered and highly ordered submicron systems. As active disordered systems medium submicron diamond and silver particles water suspensions were used. As highly ordered submicron systems the nanocomposites on the base of synthetic opal matrixes were used namely opal matrix with average size of globules 250 nm. The SLFRS parameters were measured using a conventional scheme for measuring spectral and energy characteristics [2]. To study the intracavity generation of SLFRS, we used an experimental setup based on a ruby laser operating in the Q-switching mode (Fig.1).

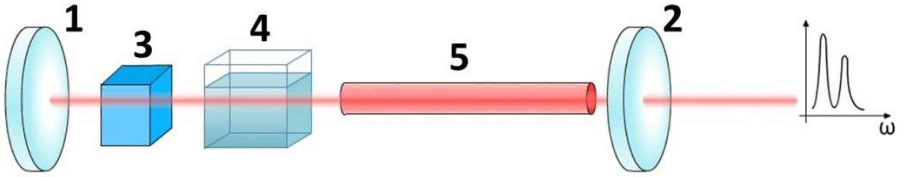

Fig. 1. 1, 2 mirrors 3 – passive q-switch, 4 - SLFRS active sample 5 –ruby crystal

A cell 10 mm long with a suspension of silver or diamond submicron particles was placed in a laser cavity between a ruby crystal and a passive Q-switch. The cavity length was 0.5 meters. The laser pulse duration in the absence of a sample in the cavity was 20 ns. The energy of the laser pulse, its duration and the spectral composition of the radiation were controlled. The multiorders (up to three orders) intracavity SLFRS generation was realized. The inracavity SLFRS spectral characteristics are proved to be in good acordance with those measured in the set up with external excitation and calculated using the Lamb theory. The obtained experimental results show the possibility of using intracavity SLFRS both for the analysis of the morphology of nanoscale and submicron systems, and as a radiation source with a given spectral distribution.

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Webinar presentation

Mid-Infrared Pumped Laser-Induced Gratings in CH_4-containing Gas Mixtures

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The mid-IR spectral range is of particular interest for combustion diagnostics: many relevant molecular species, with a key role in the reactions involved (e.g., hydrocarbons or H_2O), lack easily accessible electronic transitions in the UV- and visible spectral ranges, but resonantly absorb radiation via strong and specific mid-IR rovibrational transitions in fundamental and combinational bands. Thus, these species can be selectively probed with a high sensitivity using narrowband frequency-tunable radiation.

Methane, CH_4, is the most thermally stable saturated hydrocarbon. It is abundant in planetary objects, participate in vital activity and in gas reactions, and is used for numerous chemical and technological processes both as raw material and as common and industrial fuel. Highly symmetric tetrahedral CH_4 molecules have been thorougly investigated spectroscopically – as model molecules, in intramolecular interactions, and in collisional *V-V* and *V-T* relaxation. Local temporally- and spatially-resolved highly-sensitive diagnostics of CH_4 molecules themselves or as unseeded probe molecules in reactive gas media, in a broad range of temperatures and pressures, is of great practical interest. It is these opportunities which the laser-induced grating (LIG) technique [1,2] is able to provide, while a few parameters can be obtained in a single laser pulse measurement.

The physical and methodological aspects of the LIG technique as applied to molecular gases are known in general, and earlier the method has been already tried at mid-IR excitation of molecules [3-6]. The present work is aimed to further develop the approach through the use of a tunable narrowband OPO emitting nanosecond pulses of radiation at ~ 3 μm to generate LIGs at resonant excitation of a definite T_d component of a selected *P*-, *Q*-, or *R*- branch rovibrational transition of the ν_3 fundamental band of CH_4.

The temporal profiles of the LIG signals, recorded using CW radiation in the visible spectral range, appear to be specific of the processes of collisional deactivation, radiative decay and mass diffusion of the excited probe molecules in a selected buffer gas, and of the properties (molar mass, temperature, number density, heat capacity, thermal diffusivity) of this gas. Large LIG signal amplitudes and the peculiarities of their temporal profiles in CH_4-containing gases are defined by rapid collisional release of a large amount of the internal energy, delivered by the optical excitation, in the process of vibrational energy redistribution within the manifold of the vibrational states (ν_3, $2\nu_2$, $\nu_2 + \nu_4$, $2\nu_4$) and the transition of CH_4 molecules into the lowest vibrational state ν_4.

The experiments showed that the mid-IR excitation of CH_4 molecules allows the high sensitivity of the LIG technique at small CH_4 concentrations (~ 50 ppm in N_2 at ambient pressure and temperature) to be realized, as well as to use CH_4 as an efficient probe molecule in gas mixtures, with no influence on mixture properties. The measurements in a heatable (up to ≈ 800 K) tube have expectedly shown a good sensitivity of LIG signal profiles to temperature, which provides the possibility of thermometry up to high temperatures about 1500-1800 K, characteristic for CH_4 pyrolysis. The analysis of the LIG signal profiles recorded at different buffer gas pressures (1-8 bar) have confirmed profiles' high sensitivity to variations of pressure and the feasibility to define pressures from the signal shape. Measurements in various buffer gases, especially H_2, CO_2, and C_2H_4, which provide high collisional relaxation vibrational energy release rates, enhance LIG signal amplitude and condition a buffer gas specific signal temporal profile, have demonstrated the possibility to obtain diagnostic information while modeling the signal profile, accounting for the specific relaxation rates.

The results of the study indicate that the mid-IR-pumped LIGs technique may be developed into an efficient diagnostic tool for gas dynamic studies in hot CH_4-containing reactive gaseous media.

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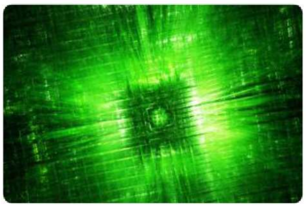

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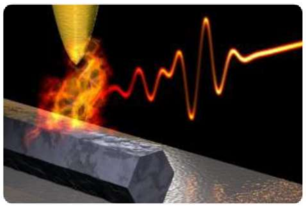

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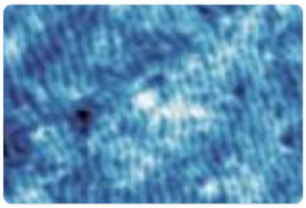

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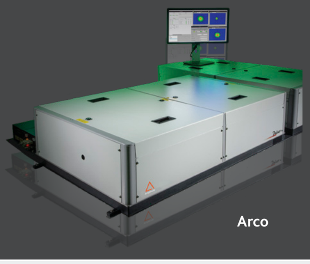
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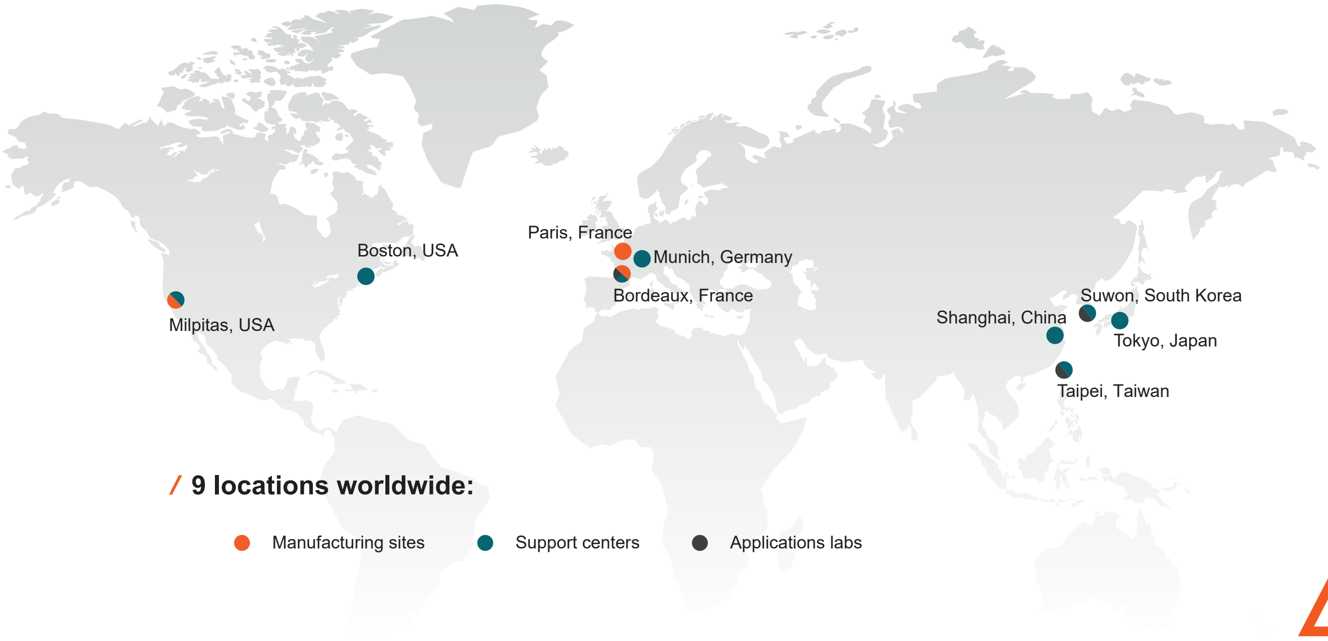

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