

## MO 1: Vibrational Spectroscopy

Time: Monday 10:30–12:45

Location: V38.03

## Invited Talk

MO 1.1 Mon 10:30 V38.03

**Vibrational Molecular Interferometry** — ●HERMAN L OFFERHAUS<sup>1</sup>, ERIK T GARBACKI<sup>1</sup>, SHAUL MUKAMEL<sup>2</sup>, ALEXANDER CW VAN RHIJN<sup>1</sup>, CEES OTTO<sup>3</sup>, and JENNIFER L HEREK<sup>1</sup> — <sup>1</sup>Optical Sciences group, University of Twente, the Netherlands — <sup>2</sup>Department of Chemistry, University of California, Irvine, USA — <sup>3</sup>Medical Cell BioPhysics group, University of Twente,

We demonstrate an implementation of a CARS microscopy method that is based on an interaction picture centered on the molecules, as proposed in [1], rather than the interacting fields. It provides an intuitive and unified description of the various signal contributions, allowing easy extraction of the vibrational response. Three optical fields create a pair of Stokes Raman pathways that interfere in a single vibrational state. Frequency modulating two of the fields leads to amplitude modulations of the signals, which we refer to as vibrational molecular interferometry (VMI). The modulation depth that we observe is comparable to that found in SRS, and allows imaging at high speed free of the non-resonant background that plagues coherent anti-Stokes Raman scattering (CARS) measurements. The demonstration is on a narrowband system and does not offer a large improvement in practical terms over existing SRS strategies, except that it can distinguish between electronic and vibrational transitions and avoids signals from Kerr-lensing. The new strategy is not limited to narrowband CARS and broadband extensions are possible. [1] Rahav, S. & Mukamel, PNAS 107, 4825-4829,(2010).

MO 1.2 Mon 11:00 V38.03

**The full characterization of the third-order nonlinear susceptibility using single-beam-CARS** — ●ALEXANDER WIPFLER, JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Single-beam-CARS setups circumvent the experimental challenge of superposing two laser pulses in space and time. However the information on the nonlinear susceptibility is often poor compared to conventional CARS and spontaneous Raman measurements. We present a method that allows for the full characterization of the susceptibility by introducing a phase gate in the excitation spectrum. The phase of this gate is subsequently set to four different values which makes a double quadrature spectral interferometry (DQSI) operation possible. This operation delivers amplitude and phase of the third-order nonlinear susceptibility. The theoretical background including simulations of the scheme and experimental results on toluene will be presented. As amplitude and phase are obtained, the information on the susceptibility gained with our method exceeds the one from conventional CARS experiments and even spontaneous Raman measurements.

MO 1.3 Mon 11:15 V38.03

**Multimodal non-linear imaging with shaped femtosecond pulses** — ●JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Multimodal non-linear imaging takes advantage of the simultaneous generation of different optical signals, like second and third harmonic generation (SHG and THG), two-photon excited fluorescence (2PEF) and four-wave mixing (FWM). SHG and THG highlight structured molecules and interfaces, whereas 2PEF is generated by specific fluorophores. FWM, on the other hand, provides contrast based on the specific third-order nonlinear susceptibility. A promising way to improve multimodal non-linear imaging is phase and amplitude shaping of the excitation pulses. Contrast and selectivity can be improved by addressing specific fluorophores emitting in the same spectral region or even by retrieving the Raman information. This work in based on the phase and amplitude shaping of a single beam from a broadband Ti:Sapphire oscillator applied to microspectroscopy. A first benchmark is presented by comparing the effect of standard Taylor-phase distortions on the different non-linear signals. The separation of spectrally overlapping 2PEF and FWM signal is studied in a plant cell. We also discuss the effect of optimization of SHG or FWM using imaging of a tendon from a rat-tail.

MO 1.4 Mon 11:30 V38.03

**Quantitative data analysis in hyperspectral CARS imaging** — ●GREGOR HEHL<sup>1</sup>, ALEXANDER KOVALEV<sup>2</sup>, and ANDREAS VOLKMER<sup>1</sup> — <sup>1</sup>3. Physikalisches Institut, Universität Stuttgart — <sup>2</sup>Department of Zoology, Christian-Albrechts-Universität Kiel

Hyperspectral coherent anti-Stokes Raman scattering (CARS) imaging, the combination of spectrally and spatially resolved CARS detection, offers access to the full wealth of chemical and physical structure information encoded in vibrational signatures of chemical species on the sub-micron length-scale. Because of the coherent nature of the CARS process, a complex spectrum of the third-order nonlinear susceptibility is probed. However, the actual measurement of the CARS spectrum yields its power spectrum. In order to reconstruct the linear Raman response of the sample a spectral phase retrieval is necessary. Two different methods for the qualitative phase-retrieval have been proposed, that is the maximum entropy method (MEM) and the Kramers-Kronig transform. In this work, we demonstrate the full quantitative reconstruction of Raman responses of skin model lipids based on MEM. We show that identical information is obtained from CARS and spontaneous Raman spectra provided that the full coherent nature of the CARS experiment is taken into account. The proposed analysis scheme for hyperspectral CARS data allows fast chemical imaging of living cells and tissues in a label-free and fully quantitative manner.

MO 1.5 Mon 11:45 V38.03

**Coherent Anti-Stokes Raman Scattering (CARS) with tunable broadband excitation and narrowband probe pulse** — ●MATTHIAS LÜTGENS, SUSANA CHATZIPAPODOPOULOS, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, 18055 Rostock

Coherent anti-Stokes Raman scattering (CARS) spectroscopy is a powerful tool to investigate vibrational modes and their pure dephasing parameters. We present a CARS technique which involves a broadband, coherent excitation of one or several vibrational modes covering a broad range of vibrational frequencies via a femtosecond, broadband Stokes and a narrowband Raman pump beam. The coherent superposition is probed with a narrowband probe beam in the ps range. For this purpose we developed a narrowband ps - non-collinear optical parametric amplifier (NOPA) that allows us to measure CARS time traces with significant higher spectral resolution compared to other fs-CARS setups without losing the ability to monitor dephasing times by the use of time-delayed probe pulses. The capability of the here presented setup is demonstrated by applying this method to different model systems. We show characteristic CARS spectra including numerical simulations of the signal that allows the determination of the energetic position of vibrational modes as well as the dephasing time  $T_2$ .

MO 1.6 Mon 12:00 V38.03

**FTIR- and Ramanspectroscopy of Substituted Paracyclophane Molecules** — ●JÖRG HERTERICH, SUSANNE ZEISSNER, INGO FISCHER, and THIEMO GERBICH — Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg

The vibrational structures of three paracyclophanes were investigated, ortho-dihydroxy-[2.2]paracyclophane (o-DHPC), monohydroxy[2.2]paracyclophane (MHPC) and 2,11-dithia[3.3]paracyclophane.

Gas-phase infrared spectroscopy helps to identify the most stable isomer in the gas phase, while FT-Raman spectroscopy permits to study the low-frequency vibrations that give insight into the pi-pi-interactions of the molecules. For o-DHPC the IR spectrum confirms that the EZ rotamer dominates, while for MHPC the spectra indicate a larger contribution of the Z rotamer than expected. The Raman spectrum of 2,11-dithia[3.3]paracyclophane showed a dominance of the trans isomer. The Raman spectra also show that the wavenumber of the lowest frequency twist mode is overestimated by density functional theory in all three molecules.

MO 1.7 Mon 12:15 V38.03

**IR spectroscopy on liquid hydrogen isotopologues** — ●ROBIN GRÖSSLE — KIT (Karlsruhe Institute of Technology), Institute for

Technical Physics - Tritium Laboratory Karlsruhe, Germany

Future fusion facilities like **ITER** and **DEMO** will have huge amounts of tritium and deuterium circulating in their systems as fuel for the fusion plasma. The  $T_2$  inventory of first generation power plants will be about 2 to 3 kg, with a throughput of approx. 1 kg per hour. One important capability of the  $T_2$  cycle is to reprocess unburned fuel and to purge tritium and deuterium. For hydrogen isotopologue processing the **Isotope Separation System (ISS)** is available, applying a cascade of cryogenic distillation columns to enrich the  $T_2$ .

Before reinjecting the tritium back to fusion process, its purity has to be measured without disturbing the distillation process. IR-spectroscopy is being examined as a reliable; reproduceable, fast and non invasive analytic technique for composition analysis of liquid hydrogen mixtures.

There are several major challenges on the way to a reliable IR measurement method: On the one hand the hydrogen sample has to be cooled to temperatures of about 20 Kelvin. And on the other hand the IR source and the detector are at room temperature. So enough cooling power and a sufficient thermal insulation are required. But also the analysis of IR spectra is not straight forward due to the overlap of spectral features from the six ( $H_2, HD, D_2, HT, DT, T_2$ ) hydrogen molecules.

MO 1.8 Mon 12:30 V38.03

**Raman Studies of Ionic Liquids with Weakly Coordinating Anions** — SUSANA CHATZIPAPADOPOULOS<sup>1</sup>, ●FRANK FRIEDRISZIK<sup>1</sup>, DANIELA KERLÉ<sup>2</sup>, OLIVER KÜHN<sup>1</sup>, STEFAN LOCHBRUNNER<sup>1</sup>, RALF LUDWIG<sup>2</sup>, MATTHIAS LÜTGENS<sup>1</sup>, and CHRISTIAN ROTH<sup>2</sup> — <sup>1</sup>University of Rostock, Institute of Physics — <sup>2</sup>University of Rostock, Institute of Chemistry

The role of hydrogen bonds in ionic liquids (ILs) is subject of intensive current research. Imidazolium-based ILs show clear hints for hydrogen bonds [1]. In addition Lassègues et al. [2] argue that overtones of the aromatic ring chain vibrations interact with C-H groups in the ring in case of weakly coordinating anions and can explain IR and Raman spectra without involving hydrogen bonds. To clarify the interpretation of vibrational spectra in the regions of the C-H stretch modes of the alkyl chain and the imidazolium ring we investigate ILs by linear Raman and IR spectroscopy. Time-resolved measurements characterizing dephasing processes are done by coherent anti-Stokes Raman spectroscopy (CARS). First experimental results will be presented and discussed in the light of molecular dynamics simulations and quantum chemical calculations.

[1] K. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* 2008, 47, 8731 - 8734

[2] J.-C. Lassègues, J. Gronding, D. Cavagnat, P. Johansson, *J. Phys. Chem. A* 2009, 113, 6419 - 6421