

MO 15: Linear and nonlinear Raman Spectroscopy

Time: Wednesday 14:30–16:15

Location: MER 02

Invited Talk

MO 15.1 Wed 14:30 MER 02

Raman spectroscopy: An indispensable tool for bio- and material photonics — ●JÜRGEN POPP^{1,2}, MICHAEL SCHMITT¹, BENJAMIN DIETZEK^{1,2}, ROBERT MÖLLER², CHRISTOPH KRAFFT², and PETRA RÖSCH¹ — ¹Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, Helmoltzweg 4, 07743 Jena — ²Institut für Photonische Technologien e.V. Jena, Albert-Einstein-Straße 9, 07745 Jena

Raman spectroscopy has established itself as an extremely capable method in almost all natural scientific disciplines. The renaissance of Raman spectroscopy was mainly triggered by the progress in laser technology and the development of sensitive detectors. Within this contribution we report about the development and application of innovative linear and non-linear Raman technologies (resonance Raman, SERS, CARS etc.) for bio- and material photonics. The activities within biophotonics deal with the localization, identification and structural analysis of biomolecules, bioparticles (e.g. bacteria, yeast, viruses) as well as biological tissue for biomedical diagnostics as well as for environmental and food analysis. The focus within material photonics lies on the characterization of the Franck-Condon point of photoactive systems (e.g. photo catalysts) by means of resonance Raman spectroscopy. The investigation of the Franck-Condon point of photochemical reactions is of utmost importance since it is the starting point for all subsequent electronic relaxation steps and therefore determines the efficiency of a photoreaction.

MO 15.2 Wed 15:00 MER 02

Investigation of the Interaction of a Group IV Transition Metal-Containing Polyoxometalate with H₂O₂ Using Raman Spectroscopy — ●AWATEF S. ASSRAN, GHADA AL-KADAMANY, NATALYA V. IZAROVA, RASHA HASSANEIN, ARNULF MATERNY, and ULRICH KORTZ — Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

Raman spectroscopy is a powerful and fast technique for the identification of molecules based on their vibrational “fingerprint”; it is also sensitive to changes in the bond structure. We report the application of Raman spectroscopy to Polyoxometalates (POMs). POMs are discrete metal-oxygen clusters with a large structural and compositional diversity and a unique combination of properties. POMs are able to activate readily available and ecologically clean oxidants: hydrogen peroxide and dioxygen. Such properties render POMs very attractive for application in heterogeneous and homogeneous catalysis, material science, and medicine. Recently, we have synthesized a novel Ti-containing [Ti₂(OH)₂As₂W₁₉O₆₇(H₂O)]₈-POM, which has shown very interesting catalytic properties. In particular, this polyanion was very active and selective in the epoxidation of alkenes, especially cyclohexene with aqueous H₂O₂. The investigation of the interaction of the polyanion with hydrogen peroxide using Raman spectroscopy provided evidence of the formation of a Ti-peroxo species. In oxidation reactions, the peroxo complex formation is followed by an oxygen transfer to the organic substrate according to the proposed mechanism.

MO 15.3 Wed 15:15 MER 02

Raman and IR Spectroscopy of Carbonic Acid Isotopologues — ●CHRISTIAN MITTERDORFER¹, JUERGEN BERNARD¹, KATRIN WINKEL^{1,2}, MARION BAUER², FREDERIK KLAUSER¹, ERWIN MAYER², and THOMAS LOERTING¹ — ¹Institute of Physical Chemistry, A-6020 Innsbruck, Austria — ²Institut of General, Inorganic & Theoretical Chemistry, A-6020 Innsbruck, Austria

Owing to the ready decomposition in water and carbon dioxide, carbonic acid (H₂CO₃) seemed to be an instable molecule for a long time.[1] But in 1993 Mayer et al. synthesized a “stable” form of carbonic acid by protonation of bicarbonate and they characterized the solid through FTIR-spectroscopy.[2] Several studies pointed out carbonic acid’s astrophysical relevance [3,4].

Here we present IR and Raman spectra of both crystalline polymorphs and their ¹³C and D isotopologues, which allow us to draw a conclusion concerning their structural symmetry. The rule of mutual exclusion indicates the presence of a center of inversion for the Beta-polymorph [5], but not for the Alpha-polymorph. Therefore the cyclic carbonic acid dimer is assumed as the building block (unit) for Beta-carbonic acid [5], whereas the Alpha-form is assumed to be built

from monomeric carbonic acid.

[1]T. Loerting et al., ChemPhysChem 2010, 11, 2305-2309 [2]W. Hage et al., Journal of the American Chemical Society 1993, 115, 8427-8431 [3]M.H. Moore et al., Spectrochimica Acta Part A 2001, 843-858 [4]W. Hage et al., Science 1998, 279, 1332-1335 [5]I. Kohl et al., Angewandte Chemie International Edition 2009, 48, 2690-2694

MO 15.4 Wed 15:30 MER 02

Complex Concentration Dependence of Glycine-Induced Structural Modification of Silver Nanoparticles Investigated by UV-VIS, SERS, and TEM — ●PATRICE DONFACK¹, ANIMESH K. OJHA^{1,2}, and ARNULF MATERNY¹ — ¹Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — ²Department of Physics, Motilal Nehru National Institute of Technology, Allahabad, India

In this contribution, we report a complex concentration-dependence of surface-enhanced Raman scattering (SERS) and UV-VIS absorption of Ag-nanoparticles (AgNPs) mixed with glycine (Gly). Surprisingly, while decreasing the Gly concentration, a new band in the UV-VIS absorption spectrum of AgNPs/Gly mixtures is found, which is red-shifting with increasing intensity, until a turning point at a critical concentration is reached. Upon further dilution of Gly, the new band blue-shifts with decreasing intensity. Similarly, the SERS intensities of the Gly bands at 615 and 905 cm⁻¹ consistently increase with decreasing Gly concentrations, reaching maxima at the critical concentration point. This agrees consistently with the variation in position and intensity of the newly developing plasmon absorption band. Interestingly, transmission electron microscopy (TEM) reveals Gly-mediated modifications of AgNPs, which includes a re-assembling and an increasing aspect ratio with decreasing Gly concentration.

MO 15.5 Wed 15:45 MER 02

Picosecond supercontinuum-based hyperspectral CARS imaging — ●S. GOMES DA COSTA, G. HEHL, and A. VOLKMER — 3. Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart

Hyperspectral coherent anti-Stokes Raman scattering (CARS) imaging has been demonstrated to provide both spatially and frequency resolved vibrational spectroscopy with sub-micron and 5-cm-1 resolutions, respectively, within complex heterogeneous samples. In previous realizations of multiplex CARS microscopy, narrowband pump- and probe pulses and a broadband femtosecond or supercontinuum (SC)-based Stokes pulse have been used in CARS process. The SC is conventionally generated in a highly nonlinear photonic crystal fibre (PCF) using a femtosecond seed pulse. As a consequence, the Stokes-continuum and the narrowband pump pulses are temporally mismatched, resulting in inefficient CARS-continuum generation. To optimize CARS, matching the temporal widths of both the pump and Stokes-continuum pulses and the spectral widths of the picosecond pump pulse and the vibrational bandwidth of interest are required. Here, we report on the first experimental realization of vibrational bandwidth-matched picosecond supercontinuum-based hyperspectral CARS imaging using a single Ti:sapphire laser oscillator with 3-ps near-transform-limited pulses. In addition to XFROG-CARS measurements, we demonstrate the increased CARS detection sensitivity, the spatial, and the spectral resolutions of our novel setup by performing three-dimensional hyperspectral CARS imaging on well-defined test samples.

MO 15.6 Wed 16:00 MER 02

Shaper Assisted Multiplex CARS — ●JEAN REHBINDER, CHRISTOPH POHLING, TIAGO BUCKOP, and MARCUS MOTZKUS — Physikalisches-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Coherent Anti-Stokes Raman Scattering (CARS) is one of the most specific non-linear effects, able to produce microscopical chemical maps without any label. Compared to its spontaneous counterpart, the coherent nature of CARS gives rise to stronger signals and hence an increase of the speed of acquisition. A limiting factor for this speed then becomes the CCD detector used to acquire whole spectra. Video-rate capabilities of CARS have been demonstrated when probing a single Raman level, sacrificing, however, chemical specificity for speed. Here we present a new scheme suited for single-channel as well as for

spectrally-resolved applications [1]. In this approach, we exploit the fact that the excitation probability for Raman modes is directly proportional to the spectral intensity of the broadband Stokes pulse in a Multiplex CARS setup. By use of an amplitude shaper we gain full control of the excited levels across the whole spectral range, where modes

from 400 cm^{-1} to 3100 cm^{-1} can be selected with a resolution of 7 cm^{-1} . The method is illustrated by imaging a polymer blend containing polystyrene, polyethylene and polymethylmethacrylate with close, partly overlapping bands selected only by the shaper. [1] Rehbinder, J. et al., Optics Letters 35 (2010) 3721.