

MO 13: Probing Vibrations

Time: Thursday 11:00–13:00

Location: N 6

Invited Talk

MO 13.1 Thu 11:00 N 6

Ultrafast solvent fluctuations steer the hydrated excess proton in the Zundel cation H_5O_2^+ — ●FABIAN DAHMS¹, RENE COSTARD¹, EHUD PINES², EVA MARIA BRÜNING¹, TORSTEN SIEBERT¹, BENJAMIN P. FINGERHUT¹, ERIK T. J. NIBBERING¹, and THOMAS ELSÄESSER¹ — ¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2a, 12489 Berlin, Germany — ²Department of Chemistry, Ben Gurion University of the Negev, P.O.B. 653, Beersheva 84105, Israel

Hydrated protons are a key feature of biochemical systems. Not only do they mediate charge transport in aqueous environments but also play a key role in cell respiration. The Zundel cation represents a prototype species in which a proton is hydrated by two water molecules. By two-color femtosecond pump-probe measurements we were able to dissect the so-called Zundel infrared absorption continuum from the OH stretching and bending vibrations^[1]. In combination with theory, this led to a new picture where ultrafast solvent fluctuations modulate the position of the central H⁺ atom in the Zundel cation (H_5O_2^+) causing the extreme broadening of infrared absorption. For the first time we investigate the dynamical behaviour of the O–H⁺–O proton transfer coordinate with femtosecond two-dimensional infrared spectroscopy. First results suggest ultrafast spectral diffusion, frequency shifts and vibrational lifetimes on a sub-100 fs time scale. In combination with results from pump-probe spectroscopy and theory, this gives new insight into vibrational motions of the hydrated proton itself. [1]: Dahms, Fabian, et al., *Angew. Chem. Int. Ed.* 55 (2016): 10600.

MO 13.2 Thu 11:30 N 6

Ultrafast dynamics of interfacial water following UV photo-excitation of TiO₂ — SAMAN HOSSEINPOUR, SIMON SCHLEGEL, SHUMEI SUN, and ●ELLEN BACKUS — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz

Hydrogen generation through photo-dissociation of water on the surface of TiO₂ has attracted profound attention over the past decades. Nevertheless, the molecular mechanism of the water splitting reaction has remained largely unresolved. The investigation of water during the water splitting reaction requires a surface sensitive tool which can probe the evolution of water molecules at the TiO₂ surface upon UV irradiation. In this study we exploit the inherent surface-sensitivity of sum-frequency generation (SFG) spectroscopy to probe the water molecules at the interface between bulk water and TiO₂. Femtosecond time-resolved SFG allows us to record changes in the orientation and hydrogen bonding interaction of interfacial water, as a function of the time following a UV pump pulse. Our preliminary results indicated a strong pH dependence of the relaxation/re-orientation of the water molecules after UV-irradiation of the TiO₂.

MO 13.3 Thu 11:45 N 6

The primary photochemical processes upon laser flash photolysis of a puckered ferrocyclobutadiene in liquid solution studied by ultrafast femtosecond mid-infrared spectroscopy — ●BORIS WEZISLA, JÖRG LINDNER, and PETER VÖHRINGER — University of Bonn

The primary photoprocesses after laser flash excitation of the novel puckered ferrocyclobutadiene, $[\text{Fe}\{\kappa^2\text{-C}_3(\text{NET}_2)_3\}(\text{CO})_3]\text{BF}_4$, are explored using femtosecond time-resolved infrared spectroscopy in conjunction with extensive signal deconvolution and quantum mechanical computations, in an effort to fathom the possibility of utilizing this class of metallacyclobutadienes as efficient alkyne metathesis catalysts.

Signal deconvolution uncovers two short lived key intermediates for the primary substitution of a single CO ligand by an acetonitrile solvent molecule, which we already discovered in a previous study with nanosecond time-resolution [1]. These intermediates are assigned by comparison with DFT calculations to the triplet ground state of the precursor molecule and a formally octahedral, planarized ferracycle with an associated explicit solvent, respectively. By inclusion of the analytical solution of a kinetic model into the global fitting routine, reaction rates for elementary steps in the photochemical relaxation are determined, which explain the origin of the low and excitation wavelength dependent primary quantum yield of less than 25%.

[1] J. Torres-Alacan, B. Wezislá, M. Straßmann, A. C. Filippou,

P. Vöhringer, *Chem. Eur. J.*, **2015**, 21, 17184-17190.

MO 13.4 Thu 12:00 N 6

Effects of fractional charges on vibrational shifts of IR and Raman-active modes using Density Functional Theory — ●REYHANEH GHASSEMIZADEH¹ and MICHAEL WALTER^{1,2} — ¹Institute of Physics, University of Freiburg, 79104 Freiburg, Germany — ²Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), 79110 Freiburg, Germany

Organic molecules, such as polycyclic carbohydrates, are promising for future use in a new generation of solar cells. To investigate electronic structure and charge transfer characteristics of these molecules, we apply (Time-dependent) Density Functional Theory (TD-DFT).

In this work we focus on interactions between charge carriers and molecular vibrations in different carbon-based molecules with various intramolecular symmetries. Due to addition of fractional charges, our studies indicate, that vibrational frequencies $\omega(q)$ are changing compared to the natural species. We present the dependency of vibrational shifts of IR- or Raman-active modes on added fractional charges. An outlook about Raman-active vibrational shifts as finger print of charge transfer in donor-acceptor complexes in a common study with experimental collaborators is given.

MO 13.5 Thu 12:15 N 6

Study of the self-reaction products of benzyl radicals via IR/UV ion-dip-spectroscopy — ●FLORIAN HIRSCH¹, PHILIPP CONSTANTINIDIS¹, INGO FISCHER¹, and ANOUK M. RIJS² — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institute for Molecules and Materials, Felix Laboratory, Radboud University, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands

The self-reaction products of benzyl radicals produced by flash pyrolysis have been studied by ion-dip-spectroscopy in a free jet. Due to the high stability of this species and its great abundance in hot flames during combustion processes, these radicals might play an important role in the formation of polycyclic aromatic hydrocarbons (PAHs) and consequently soot. Because of the potential health and environmental impact of these undesired products, it is of significant importance to understand the basic mechanisms which lead to these molecules in hot flames.

The spectroscopic method utilized in this study is capable of providing mass selective infrared spectra, which can be used for identification of the formed molecules. The radicals have been generated by flash pyrolysis from a nitrite precursor and ionized at fixed wavelengths at 265 or 275 nm. A tunable free electron laser provided infrared radiation in the range of 550 - 1750 cm⁻¹. Subsequent analysis of the differences in ion signals, with and without infrared excitation, resulted in the sought after infrared spectra for product identification.

MO 13.6 Thu 12:30 N 6

Enhancement of Vibrational Coherence by Excitation with Chirped Multipulses — ●ELISABETH BRÜHL, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany

To steer photochemical reactions into selected channels, the tailoring of molecular vibrations is a fundamental control knob. Vibrational coherence of the ground state can be manipulated by using chirped pump pulses via intrapulse impulsive Raman scattering [1]. Additionally, electronic near-resonant excitation with multipulses has been shown to enhance vibrational coherence in the excited state [2]. In this work, these two methods of mode selective control are combined to study the interplay of chirped pulses and multipulses on vibrational coherence and population in the electronic excited as well as in the ground state over a range of excitation spectra. This is demonstrated by systematic phase shaping of the excitation pulse in transient absorption of dye molecules. Our control results of population and vibrational coherence show a strong dependence on the excitation detuning. For example, a blue-detuned multipulse enhances the vibrational coherence and its influence linearly adds to the one of the chirp. The effects for resonant and red-detuned excitation, on the other hand, are in general less pronounced and do not follow the same trend as for blue-detuned. For a better understanding of the underlying process and the assign-

ment of ground and excited state contributions a numerical model is developed.

[1] Bardeen et al., JPC A 1998, 102, 17.

[2] Buckup et al., JPB 2008, 41, 074024.

MO 13.7 Thu 12:45 N 6

Distinguishing between silanol O-H and water O-H at the silica/water interface with time resolved SFG spectroscopy

— •JENÉE D. CYRAN¹, MICHAEL A. DONOVAN¹, JONATHAN F.D. LILJEBLAD², ERIC TYRODE², MISCHA BONN¹, and ELLEN H.G. BACKUS¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²School of Chemistry, Division of Surface and Corrosion Science, Royal Institute of Technology, Stockholm, Sweden

The surface properties of silica in contact with aqueous solutions impact a plethora of fields, including geochemical, technological, and biological. Characterizing the silica/water interface on a molecular level is crucial for understanding the adsorption and reaction of water on the silica surface. Sum frequency generation (SFG) spectroscopy, a surface selective technique, affords the ability to use molecular vibrations to characterize the silica/water interface. The vibrational spectrum of this interface reveals a high-frequency feature centered at 3680 cm⁻¹. It has been debated whether this resonance originates from a free O-H from water or from a silanol (Si-O-H) group. Here, we use time- and polarization resolved SFG to distinguish between these two, as the water O-H can clearly reorient much faster than a surface-bound silanol group.