

MO 12: Femtosecond Spectroscopy III

Time: Tuesday 14:00–16:00

Location: V38.03

Invited Talk

MO 12.1 Tue 14:00 V38.03

New insights into solution-phase chemistry under ambient conditions via ultrafast X-ray spectroscopy — ●NILS HUSE — Ultrafast Molecular Dynamics Group, Max Planck Research Department for Structural Dynamics at the University of Hamburg & Center For Free Electron Laser Science, Hamburg, Germany

The high chemical specificity and localized nature of core-level transitions combined with their sensitivity to valence charge distribution, spin-state, and nuclear motion make transient X-ray spectroscopy a powerful method to study chemical reactions. In particular, solution-phase chemistry has been investigated with time-resolved hard X-ray techniques for the past decade [1-3]; its younger soft X-ray analogue has delivered first results more recently [4-7]. Moreover, the first transient spectroscopy of aqueous solution in the X-ray water window demonstrates the feasibility of studying ultrafast processes via the Nitrogen K-edge. With attosecond sources approaching the necessary photon energies, this type of spectroscopy will allow to follow charge migration and successive chemical reactions in water with the chemical specificity and atomic resolution intrinsic to core-level transitions.

1. Chen et al., *Science* 292, 262 (2001); 2 Bressler et al., *PRL* 90, 047403 (2003); 3. Khalil et al., *JPCA* 110, 38 (2006); 4. Wernet et al., *APA* 92, 511 (2008), Huse et al., *PCCP* 11, 3789 (2009); 5. Wen et al., *JCP* 131, 234505 (2009); 6. Huse et al. *JACS* 132, 6809 (2010); 7. Huse et al. *JPCL* 2, 880 (2011).

MO 12.2 Tue 14:30 V38.03

Dynamics and structure in hydrogen bonded systems probed with resonant inelastic soft x-ray scattering — ●SIMON SCHRECK¹, KRISTJAN KUNNUS¹, WILSON QUEVEDO¹, FRANZ HENNIES², BRIAN KENNEDY², SIMONE TECHERT³, PHILIPPE WERNET¹, and ALEXANDER FÖHLISCH¹ — ¹Helmholtz-Zentrum Berlin — ²MAX-lab — ³Max-Planck-Institut BPC, Göttingen

Hydrogen bonded systems are ubiquitous in nature ranging from bonding in DNA to liquid water as a solvent and the natural medium for many chemical reactions and proteins. Often the structure and function of molecules and proteins is determined by the bonding properties in these systems. On the other hand the structure and the dynamics even of the simplest hydrogen bonded systems such as water and methanol are still the subject of controversial discussions.

We used resonant inelastic soft x-ray scattering (RIXS) at the O K-edge to study the dynamics and structure of liquid water and methanol. RIXS is an element specific and local probe of the valence electronic structure and hence very sensitive to the local geometric structure. Since the scattering process takes place in only a few femtoseconds (fs), RIXS is sensitive to dynamics on the fs-timescale. By detuning below the absorption resonance, the scattering-duration time can be reduced significantly and even shorter timescales can be investigated. Studying the angular anisotropy of the scattered photons gives information about the symmetry of the involved states.

The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 12.3 Tue 14:45 V38.03

ESIPT in 3-Hydroxyflavone and 3-Hydroxychromone: A Femtosecond Transient Absorption Study — ●KATHARINA CHEVALIER¹, MATTHIAS M.N. WOLF¹, ANDREAS FUNK³, MARKUS GERHARDS² und ROLF DILLER¹ — ¹Dept. of Physics, Univ. Kaiserslautern — ²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany — ³Institute for Buildings and Materials Chemistry, Univ. Siegen, 57076 Siegen, Germany

3-Hydroxyflavone (3HF) and its derivatives have recently gained interest as fluorescent probes in micelles, liposomes and membranes. Since the respective time constant of proton transfer after electronic excitation (ESIPT) with UV light as well as the characteristics of the fluorescence and transient absorption depend strongly on the polarity and hydrogen bonding ability of the surrounding medium it is important to understand the mechanism of energy deactivation. 3-hydroxychromone (3HC) is one of the basic chromophoric units of naturally occurring flavonoids which can form an intramolecular hydrogen bond. Studies in gas phase and in hydrocarbon solution have revealed a proton transfer in the excited state similar to 3HF but with significant differences in the emission properties. Results from condensed phase sub-picosecond

time resolved absorption spectroscopy are presented and compared to quantum chemical calculations allowing for the identification and characterization of photoinduced processes and intermediate states.

MO 12.4 Tue 15:00 V38.03

Ultrafast solvation dynamics of ferulic acid at a micellar surface — ●MAYRA STUHLREIER¹, MICHAL MALICKI¹, HENDRIK BÖHNKE¹, KATHLEEN OEHLKE², KARIN SCHWARZ², and FRIEDRICH TEMPS¹ — ¹Institute of Physical Chemistry, Christian-Albrechts-University Kiel, D-24118 Kiel — ²Department of Food Technology, Christian-Albrechts-University Kiel, D-24118 Kiel

The solvation dynamics of the anti-oxidant ferulic acid (FA) in buffered aqueous solution and in the palisade layer of CTAB micelles have been investigated by means of femtosecond time-resolved broadband fluorescence spectroscopy. Since the dipole moment of the molecules increases significantly upon electronic excitation, the solvent shell around the excited molecule in solution will rearrange to reach the energetically most favourable position according to the new dipole moment. This reorganization can be monitored by recording the emission spectra shortly after excitation, as they show a time-dependent red-shift corresponding to the stabilization of the solvated excited molecule. The time that is needed to reach the equilibrium structure of the solvated excited molecule and hence to complete the fluorescence shift is directly related to the mobility of the solvent molecules and therefore to the structure of the microenvironment of the solvated molecule. Compared with the dynamic red-shift of the emitted fluorescence in bulk water, a deceleration of the solvation dynamics of FA in micellar environment is clearly observable. This difference is attributed to the fast reorientation of the water molecules around the excited solutes, which is sterically hindered at the micellar surface.

MO 12.5 Tue 15:15 V38.03

Femtosecond mid-infrared study on the photochemistry of a CO-releasing compound in water — ●PHILIPP RUDOLF¹, FLORIAN KANAL¹, DOMINIK GEHRIG¹, JOHANNA NIESEL², TOBIAS BRIXNER¹, ULRICH SCHATZSCHNEIDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

In recent years, biological applications of CO-releasing molecules (CORMs), which may be utilized as an in-situ source for carbon monoxide, an endogenous gasotransmitter in the human body, have been demonstrated. Especially promising are water-soluble metal carbonyl complexes which can act as dark-stable prodrugs under physiological conditions. One of these compounds is the [Mn(CO)₃(tpm)]Cl (tris(pyrazolyl)methane (tpm) manganese tricarbonyl) complex which undergoes photoinduced CO release upon UV irradiation.

So far, the carbon monoxide liberation has mostly been studied on a macroscopic scale and at rather long irradiation times of several minutes. In this study we want to reveal the ultrafast primary processes of CO release and the incipient reactions involved. For this purpose, we employ time-resolved mid-infrared spectroscopy with different pump wavelengths, exposing an ultrafast dissociation process accompanied by the formation of new species. These experiments are complemented by linear spectroscopy methods and DFT calculations on the reactant as well as on a range of possible photoproducts.

MO 12.6 Tue 15:30 V38.03

Internal conversion vs. ultrafast intersystem crossing: A benchmark study on substituted cyclopenten-2-ones — ●OLIVER SCHALK^{1,2}, PETER LANG¹, GUORONG WU², MICHAEL S. SCHUURMAN², ALBERT STOLOW², and EBERHARD RIEDLE¹ — ¹BioMolekulare Optik, LMU, München — ²SIMS, Ottawa, Canada

Carbonyl groups are one of the most common functional groups in organic molecules. So far no systematic study exists to address their influence on excited state dynamics. Here we provide first insight using time-resolved photoelectron and transient absorption spectroscopy, as well as *ab initio* calculations to study the photodynamics of various substituted cyclopenten-2-ones in dependence on the solvent. We excite the molecules to the lowest $\pi\pi^*$ -state. Within 100 fs they reach an energetically lower $n\pi^*$ -state where the wavepacket bifurcates. Sev-

eral channels are open for a rapid return to the ground state, provided by conical intersections which are similar to those found in simple polyenes, including [1,2]-hydrogen migration, pyramidalization and ring opening [1]. However, experiments show that the vast majority of molecules instead perform intersystem crossing to the triplet manifold within 1-5 ps. A likely explanation for this behavior is a tilt in the conical intersection geometry induced by the carbonyl group which makes internal conversion hardly accessible for a change of potential energy surfaces. The rate for intersystem crossing is then determined by both, the relative energetic positions of the triplet and the $n\pi^*$ -state and spin orbit couplings which depend on solvent and substitution.

[1] O. Schalk et al., *J. Am. Chem. Soc.* **131**, 16451, (2011).

MO 12.7 Tue 15:45 V38.03

Time Resolved Photoelectron Photoion Coincidence Spectra of Sodium Doped Water Clusters — JAN P. MÜLLER^{1,2}, INGOLF V. HERTEL¹, and ●C.P. SCHULZ¹ — ¹Max Born Institute, Max-Born-Str. 2a, 12489 Berlin — ²Now at: TU Berlin, Institut für Optik und

Atomare Physik, Hardenbergstrasse 36, 10623 Berlin

Gas phase clusters of polar solvent molecules doped with an alkali metal atom are model systems for studying the behaviour of loosely bound metal valence electrons in a polar environment. In recent years, we have studied the lifetime of the first electronically excited state of sodium doped water clusters ($\text{Na}(\text{H}_2\text{O})_n$). It was found that the lifetime decreases rapidly with increasing cluster size down to about 100 fs for $n \geq 20$ [1]. These short lifetimes are presumably provoked by fast internal conversion, which is strongly correlated to the DOS of the intra molecular vibrations. Recently, we have performed time-resolved photoelectron photoion coincidence experiments. From the measured kinetic energy distributions of the electrons we gain more insight into the relaxation process. The results will be compared to similar measurements on negatively charged water clusters [2].

[1] H.T. Liu, J.P. Müller, N. Zhavoronkov, C.P. Schulz, I.V. Hertel, *J. Phys. Chem. A*, **114**, 1508 (2010).

[2] G.B. Griffin, R.M. Young, O.T. Ehrler, D.M. Neumark, *J. Chem. Phys.*, **131**, 194302 (2009).