

## MO 20: Femtosecond Spectroscopy 4

Time: Friday 11:00–13:00

Location: f102

MO 20.1 Fri 11:00 f102

**The primary photochemical processes of a ferracyclobutadiene in liquid solution studied by ultrafast mid-infrared spectroscopy** — ●BORIS WEZISLA, JÖRG LINDNER, and PETER VÖHRINGER — University of Bonn

Metallacyclobutadienes belong to a class of molecules, which are of particular interest in modern catalysis, since they have been shown to be key intermediates in alkyne metathesis. These reactions are important tools in the synthesis of complex molecules, drugs, and polymers. Our group recently communicated laser flash photolysis experiments combined with time-resolved Fourier-transform infrared spectroscopy of a pseudo-square-pyramidal ferracyclobutadiene (FeCBD). This study focused on the timescale of nanoseconds to milliseconds, and found a primary cleavage of an equatorial carbonyl ligand, which is subsequently replaced by the solvent molecule within the time resolution.

Here, we expand this study by exploring the primary processes leading to the formation of this solvent species after excitation of metal-to-CO CT states with 355 nm or 266 nm laser pulses. The ensuing photochemical processes are detected in a time- and frequency-resolved manner using femtosecond mid-infrared (fs-MIR) spectroscopy in the carbonyl stretching region (1900–2100  $\text{cm}^{-1}$ ). The spectro-temporal evolution of the transient signal reveals that the primary events are complete within 300 ps. The primary quantum yield for the formation of a FeCBD featuring a solvent molecule in the equatorial binding site is found to be less than 20%. The results are discussed in terms of TD-DFT and extensive modeling of the time-dependent mid-IR response.

MO 20.2 Fri 11:15 f102

**XUV Transient Absorption Spectroscopy of Photochemical Reactions** — ●LORENZ DRESCHER, MARTIN GALBRAITH, GEERT REITSMA, JUDITH DURA, OLEG KORNILOV, SERGUEI PATCHKOVSKII, MARC VRAKING, and JOCHEN MIKOSCH — Max-Born-Institut, Berlin, Germany

Transitions of atomic core orbitals into unoccupied molecular valence orbitals offer a site-specific view of chemical binding [1]. Spectrally, such resonant transitions are located just below the inner-shell ionization edges. Recent advances in generation of XUV pulses from High Harmonic Generation (HHG) allow to probe such molecular core-to-valence transitions in transient absorption spectroscopy at ultrafast time resolution in a tabletop setup [2]. In our experiment, methyl iodide and iodobenzene photodissociations have been excited by 266 nm femtosecond laser pulses and the transient absorption spectra at the 4d-pre-edge of iodide have been measured using quasi-continuous XUV spectra from HHG driven by sub-6 fs NIR pulses. Our results show the rearrangement of the valence shell after excitation and how the electronic states involved in photodissociation differ for iodobenzene and methyl iodide molecules.

[1] J. Stöhr, *NEXAFS Spectroscopy*, Springer (1992)

[2] Attar et al., *JCP* 141, 164308 (2014)

MO 20.3 Fri 11:30 f102

**Calculation of 2D electronic spectra using a stochastic Schrödinger equation approach** — ●PANPAN ZHANG and ALEXANDER EISFELD — MPIPES Dresden

The hierarchy of pure states (HOPS) [1] is a powerful approach to calculate the dynamics of an open quantum system using stochastic trajectories. We show that HOPS can be used in combination with phase cycling methods [2] to calculate two-dimensional electronic spectra.

[1] D. Suess et al; *Phys. Rev. Lett.* 113, 150402 (2014)

[2] P. Tian et al; *Science*. 300, 1553 (2003)

MO 20.4 Fri 11:45 f102

**Nonperturbative calculation of phase-modulated wave packet interferometry** — ●ZENGZHAO LI and ALEXANDER EISFELD — Max-Planck-Institute for the Physics of Complex Systems, Noethnitzer Str. 38, 01187 Dresden, Germany

Recent phase-modulated wave packet interferometry experiments on gases of alkaline atoms showed signals from states where multiple atoms are excited simultaneously [*Phys. Rev. A* 92, 052412 (2015)]. To shed light on the origin of these signals, we solve the Schrödinger equation for this system numerically and in addition using perturbation theory. Our calculations indicate that these signals can arise even

from non-interacting atoms.

MO 20.5 Fri 12:00 f102

**Quantum dynamics of molecular reactions in an explicit solvent cage** — ●SEBASTIAN THALLMAIR<sup>1,2</sup>, JULIUS ZAULECK<sup>1</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department Chemie, LMU München — <sup>2</sup>LS für BioMolekulare Optik, LMU München

Solvents are a crucial factor in every day chemistry. Additionally to electrostatic effects, dynamic solvent effects can emerge during ultrafast reactions with large amplitude molecular motion. We showed their importance for the photochemical bond cleavage of diphenylmethylphosphonium ions in solution [1] which is a common way to generate highly reactive carbocations.

Recently, we developed a new method combining quantum dynamics (QD) and classical molecular dynamics (MD) to model the influence of an explicit solvent environment on the QD of molecular reactions [2]. In this QD/MD approach, we extract the solvent potential from the MD trajectories by evaluating a set of different snapshots. Each solvent arrangement is taken into account individually and its potential is included in the Hamiltonian used for the QD calculations. The solute Hamiltonian is set up in specially designed reactive coordinates and the potential energy surfaces are evaluated at the ONIOM/CASSCF(10,10)/M06-2X level of theory. The solvent cage hinders the free dissociation and guides the molecular wave packet to the conical intersection which is not accessible in the gas phase. There the experimentally observed diphenylmethyl cations are formed.

[1] S. Thallmair et al., *J. Chem. Phys. Lett.* 5, 3480 (2014).

[2] S. Thallmair et al., *J. Chem. Theory Comput.* 11, 1987 (2015).

MO 20.6 Fri 12:15 f102

**Ultrafast vibrational dynamics of solvated protons** — ●FABIAN DAHMS, RENE COSTARD, ERIK T. J. NIBBERING, and THOMAS EL-SAESSER — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2a, 12489 Berlin, Germany

Over the past decades, the nature of the hydrated proton has been subject of intense study. The key roles of hydrated protons in aqueous proton transport (known as the von Grothaus mechanism), in aqueous acid-base chemistry and in proton pump membrane proteins are indisputable, yet the interconverting mechanisms and related structures such as Zundel and Eigen cations have remained elusive. With one and two color mid-infrared pump-probe spectroscopy in a range from 1500  $\text{cm}^{-1}$  up to 3700  $\text{cm}^{-1}$ , we determine the absorption bands' nature and the intrinsic vibrational lifetimes of Zundel cations on a femtosecond time scale. The extensive experimental results allow for following the energy flow and redistribution after vibrational excitation. Moreover, we gain new information about the origin of the broad Zundel absorption continuum.

MO 20.7 Fri 12:30 f102

**Photocleavage of coumarin dimers studied by UV ultrafast transient absorption spectroscopy** — ●MAN JIANG, TIAGO BUCKUP, and MARKUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität, D- 69120 Heidelberg, Germany

The photoinduced cleavage of a coumarin dimer into its two monomers is a promising mechanism for laser controlled medical applications, like the release of pharmaceutical drugs for on-demand in-vivo treatment. In order to understand the underlying dynamics of the cleavage reaction in detail and develop strategies for an increase of the reaction efficiency, UV transient absorption spectroscopy was applied to a typical coumarin dimer, 2-methylallylcarboxy-dicoumarin (linker 2). Linker 2 has an intact lactone ring structure and leads to a symmetric cleavage yielding the sole monomer product. Exciting the dimer with ultrashort pulses at 280 nm with 30 fs pulse duration, we were able to explore the precise time-scale of coumarin monomers formation and to determine the quantum yield of the dimer splitting. A branched kinetic model was developed which describes the formation of monomer and relaxation dynamics to the ground state with the corresponding rate constants. The branching ratio between the two pathways is about 1:2. Furthermore, the dependence of the dynamics of the cleavage reaction on the dimer side group substitution will be discussed.

MO 20.8 Fri 12:45 f102

**Imaging molecular dynamics in I<sub>2</sub> by strong-field ionization**

— •FLORIAN BACH, FELIX BRAUSSE, FARUK KRECINIC, ARNAUD ROUZEE, HANS-HERMANN RITZE, and MARC VRAKING — Max-Born-Institut, Berlin, Germany

We investigated the dissociating wave packet dynamics in I<sub>2</sub> molecules following excitation by a 710 nm, 50 fs, pump laser pulse into the A state. The molecular motion was mapped into the photoelectron and photoion momentum distributions resulting from strong-field ioniza-

tion by a 1300 nm probe laser pulse. Both momentum distributions were recorded with a velocity map imaging spectrometer (VMIS). The kinetic energy distribution of the I<sup>+</sup> fragments shows a clear signature of the dissociating wave packet motion induced by the pump laser pulse. We observe as well a modification of the angular distribution of the high kinetic energy photoelectrons that result from laser induced electron rescattering with the time delay between the two pulses that we assign to the change of the internuclear distance of the molecule.