

MO 23: Femtosecond Spectroscopy 3

Time: Friday 14:00–15:45

Location: BEBEL HS213

MO 23.1 Fri 14:00 BEBEL HS213

Transient grating spectroscopy with extreme ultraviolet light

— E. F. SISTRUNK¹, J. GRILJ^{1,2}, J. JEONG³, M. SAMANT³, A. X. GRAY⁴, H. A. DUERR⁴, M. KOCH⁵, S. S. P. PARKIN³, and •M. GUEHR¹ — ¹PULSE, SLAC, Menlo Park, CA 94305, USA — ²EPFL Lausanne, CH-1015, Switzerland — ³IBM Almaden Research Center, San Jose, CA 95120, US — ⁴SIMES, SLAC, Menlo Park, CA 94305, USA — ⁵Experimental Physics, TU Graz, A-8010 Graz, Austria

Transient grating spectroscopy, introduced in the optical domain for its high signal-to-noise ratio at ultrafast time-resolution, has been a successful method for studying electronic and nuclear dynamics in molecules and solids. We demonstrate the first transient grating probed by ultrashort extreme ultraviolet pulses. The extreme ultraviolet range with photon energies from 10 to 100 eV provides element sensitivity on the important 3d transition elements via their 3p-3d core-to-valence resonances. We create a transient grating on VO₂, which undergoes an insulator-to-metal transition (IMT) upon optical excitation with 800 nm pulses. The probe pulse is generated by strong field high harmonic generation (HHG) and contains photon energies at the vanadium 3p-3d transition. It probes the transient grating in a reflective geometry under grazing incidence. The first diffraction order of the transient grating shows spectrally resolved harmonics of the probe pulse. The diffraction intensity rises with a several picosecond time constant followed by a decay over >100 ps. In the talk we will discuss the different mechanisms of diffraction from the VO₂ sample and the sensitivity to electronic and nuclear rearrangements in the IMT.

MO 23.2 Fri 14:15 BEBEL HS213

Strong field ionization of Butadiene with sub-7fs laser pulses

— •SASCHA BIRKNER, FEDERICO FURCH, ALEXANDRIA ANDERSON, MARTIN GALBRAITH, JOCHEN MIKOSCH, CLAUS PETER SCHULZ, and MARC J.J. VRAKING — Max-Born-Institut, Berlin, Deutschland

Strong field ionization (SFI) is a sub-cycle spectroscopic method and underlies most other attosecond spectroscopies. In recent years, it has been shown that in polyatomic molecules not only the ionic ground state but also excited ionic states are populated during SFI [1,2,3]. By combing a high repetition 400 kHz laser system delivering sub-7 fs, 4 μJ pulses at 800 nm with a reaction microscope enabling coincident detection of ion and electron momentum, the SFI of 1,3-Butadiene has been investigated. For different ionic fragment groups distinct electron momentum distributions have been observed. Our studies are particularly sensitive to the kinetic energy release of the ionic fragments. First observations point towards statistically driven unimolecular decay of the electronically excited cation.

[1] H. Akagi, et al., Science 325, 1364 (2009).

[2] A.E. Boguslavskiy, et al., Science 335, 1336 (2012).

[3] J. Mikosch, et al., Phys. Rev. Lett. 110, 023004 (2013).

MO 23.3 Fri 14:30 BEBEL HS213

Individual surrounding effects – how a single counterion changes the photochemistry of phosphonium ions

— •SEBASTIAN THALLMAIR^{1,2}, CHRISTIAN F. SAILER², EBERHARD RIEDLE², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS Für BioMolekulare Optik, LMU München

Photochemical bond cleavage of phosphonium ion is a common tool to generate carbocations in polar and moderately polar solvents. The degree of ion pairing – hence the distance to the counterion – as well as the type of counterion influence the product formation after the bond cleavage. Ultrafast transient absorption measurements have shown, that complex counterions like SbF₆⁻ or BF₄⁻ lead to the generation of carbocations while excitation of phosphonium salts with halides (e.g. Cl⁻, Br⁻) is followed by radical formation.

First we show the influence of the different counterions on the electronic excitations at the Franck-Condon point. Whereas the anions with a high oxidation potential (e.g. SbF₆⁻, BF₄⁻) do not contribute to the lowest excited singlet states while Cl⁻ or Br⁻ reveal another behaviour. These halides are relatively easily oxidized which can be seen in their contribution to the excited states manifold via charge transfer excitations.

On the basis of these results different reaction pathways depending on the counterion are presented. Our theoretical investigations clarify that besides the design of the phosphonium precursor and the chosen

solvent the counterion is an additional control knob for the photochemical bond cleavage of phosphonium salts.

MO 23.4 Fri 14:45 BEBEL HS213

Photo induced electron transfer in a self formed aluminum corrole - viologen complex.

— •TILL STENSITZKI¹, ANGELICA ZACARIAS², ZEEVE GROSS³, ATIF MAHAMMED³, YANG YANG¹, and KARSTEN HEYNE¹ — ¹Department of Physics, Freie Universitaet Berlin, Berlin, Germany — ²Max-Planck-Institut fuer Mikrostrukturphysik und European Theoretical Spectroscopy Facility (ETSF), Germany — ³Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel

Corroles are closed tetrapyrroles similar to porphyrines, missing a C-atom at a meso position. Like porphyrines, they serve as a ligand for different metals. Furthermore, their photo-reaction is quite complex, violating Kasha's rule and showing complex and not fully understood excited state absorption.

Using polarization resolved femtosecond transient absorption and other spectroscopic methods, we show that sulfonated Al-corrole forms a complex with methyl-viologen. Upon formation of this complex, fluorescence is quenched almost completely.

Analysis of the transient absorption spectra shows viologen-radical absorption and rapid loss of excited state population. This indicates ultrafast electron transfer dynamics.

For comparison we also investigated the dynamics of the corrole without methyl viologen, which exhibits fluorescence signals with a risetime of 10 ps. Our data provide information on various significant energy relaxation pathways in these type of molecules.

MO 23.5 Fri 15:00 BEBEL HS213

Femtosecond ionization dynamics of N₂ studied by wavelength-selected XUV pulses

— •MARTIN ECKSTEIN¹, CHUNG-HSIN YANG¹, HANS-HERMANN RITZE¹, FABIO FRASSETTO², LUCA POLETTO², MARC VRAKING¹, and OLEG KORNILOV¹ — ¹Max-Born-Institut, Berlin, Germany — ²CNR-IFN, Padova, Italy

Studies of dissociative ionization of N₂ have a long history both for the purpose of atmospheric research and as tests of novel experimental methods and theoretical approaches to the problem of electron correlations. A prominent example is the inner valence photoionization of N₂ in the extreme ultraviolet (XUV) region of photon energies. The molecular electronic states in this region (30-50 eV) are strongly correlated and dissociate on femtosecond time scales. Despite the long history of research, the pose significant challenges for ab initio theories deterring complete explanation of the ionization dynamics. We present a novel approach using a time-compensating XUV monochromator in combination with an HHG source. The monochromator allows us to generate wavelength-selected femtosecond XUV pulses to initiate the dynamics, which is probed by multiphoton ionization by 800 nm. The time resolved photoelectron and photoion spectra recorded for six XUV photon energies between 32 eV and 50 eV reveal changes in branching ratios of several ionization channels, both resonant and non-resonant to the photon energy. The transient signals help us to identify major dissociative channels and follow the dynamics in real time. Preliminary ab initio calculations with extended basis sets will be presented and compared with experimental results.

MO 23.6 Fri 15:15 BEBEL HS213

Selective excitation of electronic states in K₂

— •HENDRIKE BRAUN¹, DOMINIK PENDEL², CRISTIAN SARPE¹, MATTHIAS WOLLENHAUPT², and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, 26129 Oldenburg, Germany

Recently we reported on the selective excitation of K₂ using spectrally phase-shaped femtosecond laser pulses [1]. Here we present data about the controlled excitation of the same molecule by optimized double pulse sequences [2]. In addition first experimental evidence shows that femtosecond laser pulses that are shaped with spectral phases consisting of second and third order polynomial modulation [3] offer a high degree of control over the populations in selected electronic states of the potassium dimer. A detailed analysis of quantum dynamic simulations reveals different mechanisms at play.

-
- [1] T. Bayer *et al.*, Phys. Rev. Lett. **110**, 123003 (2013)
[2] M. Wollenhaupt *et al.*, JPPA **180**, 248 (2006)
[3] J. Schneider *et al.*, Phys. Chem. Chem. Phys. **13**, 8733 (2011)

MO 23.7 Fri 15:30 BEBEL HS213

Imaging valence electron motion during pericyclic reactions via time-resolved X-ray scattering — •TIMM BREDMANN, MIKHAIL IVANOV, and GOPAL DIXIT — Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin, Germany

Shooting the ultrashort, high-resolution movie of molecular processes is a long-standing dream of physicists, chemists and biologists, the realization of which will extend the understanding and hence the con-

trolability of chemical reactions in synthesis and bioscience. Here, we show by means of quantum mechanical ab-initio simulations how time-resolved X-ray scattering can be used to achieve this goal. We introduce a new technique for reconstructing the electron density from the time-resolved scattering pattern using only information of weakly scattered photons, thereby filtering out major contributions of core and inert valence electrons, yielding direct insight into the making and breaking of chemical bonds in complex molecules. Taking the Cope rearrangement of semibullvalene as explicit example, we demonstrate that this technique provides direct experimental access to the long-standing problem of synchronous vs. asynchronous bond making and bond breaking in pericyclic reactions, which has solely been investigated theoretically up to date.