

MO 10: Highly Excited Molecules and Clusters

Time: Wednesday 14:30–16:30

Location: N 6

Invited Talk

MO 10.1 Wed 14:30 N 6

Molecular movies of migrating protons on different paths — ●HEIDE IBRAHIM¹, VINCENT WANIE¹, SAMUEL BEAULIEU¹, BENJI WALES², BRUNO SCHMIDT¹, XIAO-MIN TONG³, JOE SANDERSON², MICHAEL SCHURMAN⁴, and FRANÇOIS LÉGARÉ¹ — ¹INRS-EMT, 1650 Blvd. Lionel-Boulet, J3X 1S2, Varennes (Qc) Kanada — ²University of Waterloo, 200 University Av. West, Waterloo, Ontario, Kanada N2L 3G1 — ³University of Tsukuba, Ibaraki, 305-8577 Japan — ⁴NRC, 100 Sussex Dr, Ottawa, Ontario, Kanada K1A 0R6

How do atoms move within a molecule? What are the paths they take? Coulomb Explosion Imaging combined with a multi-color pump probe scheme allows us to address these questions with a table top setup. Since the momentum information of molecular fragments is preserved at the moment of explosion we can deduce their momentary position, representing the structure of the molecule. We have studied isomerization and dissociation events through the movement of protons, deuterons and electrons, taking advantage of the rich statistics this technique provides. In the case of proton migration in the acetylene cation we were able to identify an isotope dependent to- and fro isomerization behavior [1]. Presently, we are expanding our studies on more complex processes. Aside from passively studying dynamics, we have also actively controlled the electron localization in small molecules using two-color mid-infrared asymmetric laser fields [2].

[1] H.Ibrahim et al., *Nature commun.* 5:4422 (2014)

[2] V. Wanie et al., *J. Phys. B: At. Mol. Opt. Phys.* 49 025601 (2016)

MO 10.2 Wed 15:00 N 6

Ultrafast Isomerization in Acetylene Dication: To Be or Not To Be — ZHENG LI^{1,2}, ●LUDGER INHESTER¹, CHELSEA LIEKHUS-SCHMALTZ², ORIOL VENDRELL³, and TODD MARTINEZ² — ¹CFEL, DESY, Notkestr. 85, D-22607 Hamburg, Germany — ²SLAC National Accelerator Laboratory, CA 94025 Menlo Park, USA — ³Department of Physics and Astronomy, Aarhus University, 8000 Aarhus, Denmark

The mechanism for ultrafast isomerization of acetylene [HCCH]²⁺ to vinylidene [H2CC]²⁺ dication is nebulous. Theoretical studies show a large potential barrier (>2eV) for isomerization pathways, implying that the corresponding isomerization should take picoseconds or even longer. However a recent experiment at a femtosecond X-ray free electron laser (XFEL) suggests that large amplitude hydrogen migration proceeds on a sub-100 femtosecond time scale[1]. We present a complete theoretical study of dynamics of acetylene dication produced by Auger decay after X-ray photoionization of carbon K-shell. We find that isomerization does not occur on the sub-100 fs timescale and is not required to explain the time-resolved Coulomb imaging experiment. This study resolves the seeming contradiction between experiment and theory concerning the isomerization time scale in acetylene dication. This work calls for careful interpretation of structural information from the widely applied Coulomb momentum imaging method but also points out its strengths in mapping out momentum dispersion dynamics even when structural variation is minor[2].

[1] Ch. Liekhus-Schmaltz et al., *Nature Commun.* 6, 8199 (2015).

[2] Z. Li et al., arXiv:1605.05707, submitted.

MO 10.3 Wed 15:15 N 6

Single-Shot Pump-Probe Studies in a Two Color (V)UV Field — ●ARNE BAUMANN^{1,2}, OLIVER SCHEPP¹, DIMITRIOS ROMPOTIS³, ARMIN AZIMA¹, MAREK WIELAND^{1,2,4}, and MARKUS DRESCHER^{1,2,4} — ¹Institut für Experimentalphysik, Universität Hamburg, Hamburg, Deutschland — ²Hamburg Centre for Ultrafast Imaging - CUI, Hamburg, Deutschland — ³Deutsches Elektronensynchrotron - DESY, Hamburg, Germany — ⁴Center for Free-Electron-Laser Science - CFEL, Hamburg, Germany

To gain a complete picture of few-femtosecond (V)UV-induced reactions delay-dependent ionization of parent and fragment ions by weak probe photons is an excellent tool. The presented single-shot pump-probe scheme is based on wave-front splitting of intense harmonic radiation of a Ti:Sa laser system. Individual pulses are focused anti-parallelly into a gas target and ions created are imaged onto a position-sensitive detector, thus mapping the temporal delay between both pulses onto a spatial coordinate. By using different dielectric mirrors and/or filters for each pulse, a two-color cross-correlation and

pump-probe experiment is realized, benefiting from single-shot acquisition capabilities.

The multiphoton UV-dissociation dynamics of formaldehyde have been studied with an intense 5th harmonic (161.8 nm) probe after irradiation at 269.7 nm. The 7.7 eV probe enables studies of the delay-dependent dissociative ion-yield for various fragments of this dissociation reaction in a perturbative approach.

MO 10.4 Wed 15:30 N 6

Time-Resolved XUV-induced Electron Solvation Dynamics in Ammonia and Water Clusters — ●RUPERT MICHIELS¹, AARON LAForge¹, MATTHIAS BOHLEN¹, CARLO CALLEGARI², ANDREW CLARK³, MARCEL DRABELLS³, KEVIN C. PRINCE², STEFANO STRANGES⁴, MARCELLO CORENO⁵, PAOLA FINETTI², OKSANA PLEKAN², JUN MA⁶, VERONICA OLIVER³, HANS-JAKOB WÖRNER⁶, and FRANK STIENKEMEIER¹ — ¹Universität Freiburg, Germany — ²Eletra-Sincrotrone Trieste, Italy — ³Ecole Polytechnique Fédérale de Lausanne, Switzerland — ⁴University Sapienza, Italy — ⁵CNR - Istituto di Struttura della Materia, Italy — ⁶ETH Zürich, Switzerland

The solvation of electrons in aqueous solutions plays an important role in biological and chemical systems. Nonetheless, a fundamental understanding of its properties (e.g. solvation time, binding energies, solvation shells, and binding motifs) has yet to be fully attained. Here, we report new results for ammonia and water clusters investigating XUV ionization followed by electron recapture. The binding energies of the solvated electron were measured in a pump-probe scheme as a function of cluster size in which we found solvation times in the femtosecond to picosecond range.

MO 10.5 Wed 15:45 N 6

Multi-state Photoelectron Circular Dichroism in Femtosecond Multiphoton Ionization — ●ALEXANDER KASTNER, STEFANIE ZÜLLIGHOVEN, TOM RING, CRISTIAN SARPE, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CIN-SaT, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions (PADs) from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation. This effect was termed Photoelectron Circular Dichroism (PECD) and so far investigated using synchrotron radiation [1, 2]. We observed highly structured asymmetries in the range of +/- 10 % on bicyclic Ketones [3, 4].

Due to the multi photon ionization (MPI), high order Legendre polynomials appear in the measured PADs. In the case of Resonance Enhanced MPI (REMPI) using different intermediate states, the contributions in the photoelectron spectrum depend on wavelength. By changing wavelength and intermediate states, we are able to investigate PECD depending on photoelectron kinetic energy.

[1] I. Powis in S. A. Rice (Ed.): *Adv. Chem. Phys.* 138, 267-329, (2008)

[2] L. Nahon et al., *J. El. Spectr.* 204, 322-334, (2015)

[3] C. Lux et al., *Chem. Phys. Chem.* 16, 115-137, (2015)

[4] A. Kastner et al., *Chem. Phys. Chem.* 17, 1119-1122, (2016)

MO 10.6 Wed 16:00 N 6

Comparing UV and strong-field induced dynamics in selenophene probed by femtosecond XUV transient absorption spectroscopy — ●FLORIAN LACKNER^{1,2,3}, ADAM S. CHATTERLEY^{1,2}, C. D. PEMMARAJU^{1,4}, KRISTINA D. CLOSSER⁴, DAVID PRENDERGAST⁴, DANIEL M. NEUMARK^{1,2}, STEPHEN R. LEONE^{1,2,5}, and OLIVER GESSNER¹ — ¹Chemical Sciences Division, Lawrence Berkeley National Lab — ²Department of Chemistry, UC Berkeley — ³Institute of Experimental Physics, TU Graz — ⁴The Molecular Foundry, Lawrence Berkeley National Lab — ⁵Department of Physics, UC Berkeley

UV and strong-field induced dynamics in selenophene (C₄H₄Se) molecules are studied by femtosecond transient inner-shell absorption spectroscopy at the Se 3d edge. Spectra obtained upon strong-field ionization are dominated by emerging bare Se ions produced in a sequential two-step mechanism, whereby the initial ring-opening and the subsequent fragmentation are associated with two characteristic time-

scales of $\tau_1 \approx \tau_2 \approx 80$ fs. In contrast, excitation with a moderately intense UV (266 nm) pump pulse gives predominantly rise to the formation of bare Se atoms and a smaller contribution of Se ions. The ionic contribution increases with UV intensity. In both cases, spectral signatures of stable molecular products are found as well, which are assigned based on TDDFT calculations. Independent of the excitation/ionization scheme, the breaking of both C-Se bonds is the dominant relaxation channel in selenophene, which can be traced in real-time by XUV transient absorption spectroscopy.

MO 10.7 Wed 16:15 N 6

Time-resolved Photoionisation of the S2 ($\pi\pi^*$) State of Xanthone — ●MARCO FLOCK, HANS-CHRISTIAN SCHMITT, and INGO FISCHER — Julius-Maximilians University of Würzburg, Institute of Physical and Theoretical Chemistry, Am Hubland, 97074 Würzburg, Germany

Previous studies on Fluorenone, NDCA and Naphthalimide showed,

that relaxation processes in such aromatic heterocycles are determined by a competition between internal conversion (IC) and intersystem crossing (ISC). Which relaxation pathway is preferred depends strongly on the vibrational levels of the excited states. As a further representative of the group of aromatic heterocycles, we investigated the excited state dynamics of the S2 ($\pi\pi^*$) state of Xanthone. In a jet-cooled photoionization experiment, we resolved the vibronic properties of this state and found a defined structure with well-resolved vibronic bands. In time-resolved experiments, we found a depopulation of the S2 state with two time constants $\tau(1) < 1$ ps and $\tau(2) = 24$ ps followed by a constant signal offset, which occurs from the population of the long-lived T1 ($n\pi^*$) state. Thus, two relaxation pathways can be mentioned. In a first model, IC to the S1 ($n\pi^*$) state followed by an ISC process to the T1 ($n\pi^*$) state could take place. In another model, the first time constant belongs to a fast ISC process to the T2 ($\pi\pi^*$) state, whereas the slower time constant represents a following IC process to the long-lived T1 ($n\pi^*$) state. In both models, El-Sayed forbidden ISC processes may take place.