MO 12: Femtosecond Spectroscopy III

Time: Wednesday 10:30–13:00 Location: TOE 317

MO 12.1 Wed 10:30 TOE 317

Towards ultrafast diffractive imaging of strongly aligned complex molecules: X-ray induced radiation damage — •Lotte Holmegaard[1], Jochen Küpper[1,2,3,4], Henry Chapman[1,4], and Daniel Rolles[2] — [1]CFEL, DESY, Hamburg — [2]CFEL, MPG-ASG, Hamburg — [3]Fritz Haber Institute, Berlin — [4]University of Hamburg

Emerging X-ray Free-Electron Laser Sources such as the LCLS at SLAC or the European XFEL in Hamburg have sparked novel approaches for studying ultrafast molecular dynamics. A key interest is to use strongly aligned and oriented molecules as targets in electron or X-ray diffraction experiments. As a prerequisite for realizing such experiments we have demonstrated the first adiabatic alignment measurement established at a hard X-ray FEL. Strong molecular alignment is characterized by ionization induced by the fs X-rays pulses as well as by Coulomb explosion from a short fs NIR laser pulse. The results provide the first study of ionization and radiation damage of an adiabatically aligned large/complex molecule following X-ray absorption.

This work was carried out within a collaboration for which H. Chapman, J. Küpper and D. Rolles are spokespersons. The collaboration consists of CFEL (DESY, MPG, University Hamburg), Fritz-Haber-Institute Berlin, MPI Nuclear Physics Heidelberg, MPG Semiconconductor Lab, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI Medical Research Heidelberg, TU Berlin, Max Born Institute Berlin, and SLAC Menlo Park, CA, USA. The experiments were carried out using CAMP (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 12.2 Wed 10:45 TOE 317

Time-Resolved Photoelectron Diffraction in Laser-Aligned Molecules — •Daniel Rolles[1,2], Artem Rudenko[1,3], Jochen Küpper[4,5,6], Henry Chapman[4,6], and Joachim Ullrich[1,3] — [1]Max Planck Advanced Study Group at CFEL, Hamburg — [2]Max-Planck-Institut für medizinische Forschung, 69120 Heidelberg, Germany — [3]Max-Planck-Institut für Kernphysik, Heidelberg — [4]CFEL at DESY, Hamburg — [5]Fritz-Haber-Institut, Berlin — [6]Universität Hamburg

The Br(2p) molecular-frame photoelectron angular distributions of laser-aligned dibromobenzene molecules were measured at the Linac Coherent Light Source using a velocity map imaging spectrometer. The molecules were adiabatically aligned both in 1D and 3D by a nano-second YAG laser synchronized with the FEL. In a second step, time-resolved photoelectron diffraction patterns of these laser-aligned molecules were recorded by Coulomb exploding the molecules with a femtosecond-Ti:Sa laser pulse prior to the FEL ionization and varying the delay between Ti:Sa pump and FEL probe pulse.

This work was carried out within a collaboration between CFEL (DESY, MPG, Uni Hamburg), Fritz-Haber-Institut Berlin, MPI f. Kernphysik Heidelberg, MPI Halbleiterlabor München, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI f. medizinische Forschung Heidelberg, TU Berlin, Max-Born-Institut Berlin, and SLAC Menlo Park, CA, USA, led by D. Rolles, J. Küpper and H. Chapman. The experiments were carried out using the CAMP instrument (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 12.3 Wed 11:00 TOE 317

Femtosecond RIXS on liquid jets and first results from LCLS — Philippe Wernet[1], •Kristjan Kunnus[1], Martin Beye[1], Simon Schreck[1], Edlira Suljoti[1], Christian Weniger[1], Christian Kalus[1], Kerstin Kalus[1], Alexander Föhlisch[1], Ivan Rajkovic[2], Sebastian Grübel[2], Wilson Quevedo[2], Mirko Scholz[2], Simone Techert[2], Brian Kennedy[3], Franz Hennies[3], Dennis Nordlund[4], Robert Hartsock[5], Wenkai Zhang[5], Kelly Gaffney[5], Josh Turner[6], Bill Schlotter[6], Ida Josefsson[7], and Michael Odelius[7] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]Max-Planck-Institut für Biophysikalische Chemie — [3]MAX-lab — [4]SSRL, SLAC National Accelerator Laboratory — [5]PULSE, SLAC National Accelerator Laboratory — [6]LCLS, SLAC National Accelerator Laboratory — [7]Stockholm University

We developed a set up for femtosecond time resolved resonant inelastic soft x-ray scattering (RIXS) on liquid jets in vacuum. This allows for complete probing of occupied and unoccupied valence states of molecules in real-time during chemical reactions in solutions. Results from the first experiments at the Linac Coherent Light Source (LCLS) on the photodissociation of $Fe(CO)_5$ molecules in ethanol will be presented together with complementary results from the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 12.4 Wed 11:15 TOE 317

Polarization control in two-color above-threshold ionization of small molecules — •Torsten Leitner[1], Mateusz Ibek[1], Michael Meyer[2], and Philippe Wernet[1] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]European XFEL, Hamburg

The high-harmonic generation (HHG) setup at HZB provides high peak power ultrashort femtosecond VUV pulses. Two-color multiphoton ionization of atoms and small molecules was investigated by combining these VUV pulses with an optical laser. In the photoelectron spectrum, on both sides of the main line associated with direct ionization additional lines show up in the presence of a strong optical dressing field due to above-threshold ionization (ATI). These so called sidebands undergo strong variations of their intensity as a function of the relative polarization of the VUV and the optical field [1]. The variations showed different amplitudes for the 4 atomic or molecular systems which were investigated (Ar, N_2, O_2, H_2O). This polarization and species dependence provides direct insight into the symmetry of the outgoing electron wave and therefore insight into the symmetry of the outer shell orbitals of the bound system.

[1] M.Meyer et al, PRL 101, 193002 (2008)

MO 12.5 Wed 11:30 TOE 317

Unusual mechanism for H_3^+ formation from ethane as obtained by femtosecond laser pulse ionization and quantum chemical calculations — Peter Kraus, Martin Schwarzer, •Nora Schirmel, Gunter Urbasch, Gernot Frenking, and Karl-Michael Weitzel — Fachbereich Chemie, Philipps-Universität Marburg, Deutschland

The formation of H_3^+ from saturated hydrocarbon molecules represents a prototype of a complex chemical process, involving the breaking and the making of chemical bonds. We present a combined theoretical and experimental investigation providing for the first time an understanding of the mechanism of H_3^+ formation at the molecular level.[1] The experimental approach involves femtosecond laser pulse ionization of ethane leading to H_3^+ ions with kinetic energies on the order of 4 to 6.5 eV. The theoretical approach involves high-level quantum chemical calculation of the complete reaction path. The calculations confirm that the process takes place on the potential energy surface of the ethane dication. A surprising result of the theoretical investigation is, that the transition state of the process can be formally regarded as a H_2 molecule attached to a $C_2H_4^{2+}$ entity but IRC calculations show that it belongs to the reaction channel yielding $C_2H_3^+ + H_3^+$. Experimentally measured kinetic energies of the correlated H_3^+ and $C_2H_3^+$ ions confirm the reaction path suggested by theory. [1] Peter M. Kraus, Martin C. Schwarzer, Nora Schirmel, Gunter Urbasch, Gernot Frenking and Karl-Michael Weitzel, to be published.

MO 12.6 Wed 11:45 TOE 317

Steering the electron motion in H_2^+ by nuclear wave packet dynamics — •Bettina Fischer, Manuel Kremer, Thomas Pfeifer, Bernold Feuerstein, Vandana Sharma, Nicolas Camus, Robert Moshammer, and Joachim Ullrich — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

By combining carrier-envelope phase stabilization of ultrashort (6fs) laser pulses with optical pump-probe spectroscopy the ‘left/right’ asymmetry of H^+ emission in dissociating H_2^+ molecular ions is investigated. Both, the localization and localizability of the bound electron at one or the other proton strongly depend on the time delay between the two CEP stable laser pulses revealing specific temporal signatures for different fragment kinetic energies. This delay dependence allows us to gain insight into the underlying physical mechanisms for electron localization. Two distinct sets of interfering dissociation channels can be identified by the specific temporal structure of the resulting asymmetry in the proton emission.

MO 12.7 Wed 12:00 TOE 317

CRASY: Correlated Rotational Alignment Spectroscopy Resolves Cluster Fragmentation — •Christian Schröter, Ingolf-Volker Hertel, and Thomas Schultz — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

Femtosecond-pump-probe-spectroscopy is a common tool for the investigation of structure and dynamics of electronic states in atoms, molecules and clusters. A problem with non-covalently bound clusters is the easy fragmentation either in the excited or the ionic state. As a result the spectroscopic data can*t be assigned to a specific cluster size.

CRASY is a method which combines rotational spectroscopy in the time domain with femtosecond-pump-probe experiments. An IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay, we probe the wave packet by a UV pulse which excites and ionizes the molecule via a resonant electronic state. If we detect ion-masses (mass-CRASY), the ion signal is modulated by the rotational frequencies encoded in the rotational wave packet and can be extracted by a Fourier-transform. By correlating the ground state molecular structure with the ion signals, we can resolve fragmentation pathways and assign size selected cluster data.

The CRASY method was applied to the non-linear molecule Butadiene. We observe fragmentation of non-covalent and covalent bonds in the butadiene-molecule and its clusters. With the ability to characterize ground state structure which gave rise to a mass or electron signal, mass-CRASY resolves the spectroscopic problem described above.

MO 12.8 Wed 12:15 TOE 317

Fragmentation studies of chiral molecules via femtosecond-laser mass spectrometry — •Christian Lux, Vanessa Brandenstein, Cristian Sarpe, Matthias Wollenhaupt, and Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, D–34132 Kassel, Germany

Under symmetrical conditions two enantiomers of a chiral molecule that are non superimposable mirror images of each other show almost the same physical properties. In the recent past the analysis of enantiomers based on laser irradiation using circular polarized ultrashort-laser pulses was realized for many chiral molecules.

In this contribution we investigate the effect of Circular Dichroism (CD) on the ion yields [1-4] of low-volatile chiral molecules employing femtosecond laser pulses.

CD refers to the difference between absorption of left- and right-circularly polarized light for one enantiomer and shows a specific anisotropy. Using infrared circularly-polarized laser pulses and a Wiley-McLaren time-of-flight mass spectrometer we study differences in the anisotropy of Parent-Ions and their fragments with respect to the process of Multi-Photon-Ionization-Dissociation.

As test specimen in our first experimental investigations we use the enantiomers of limonene, camphor and fenchone.

[1] U. Boesl *et al.*, Chem. Phys. Chem. 7: 2085-2087 (2006)
[2] A. Bornschlegel *et al.*, Chem. Phys. Lett. 447: 187-191 (2007)
[3] H. G. Breuning *et al.*, Chem. Phys. Chem. 10: 1199-1202 (2009)
[4] C. Logé *et al.*, Anal. Bioanal. Chem. 395: 1631-1639 (2009)

MO 12.9 Wed 12:30 TOE 317

Ultraschnelle Zerfallsdynamik von 4p-Rydberg-Zuständen des $\mathbf{CS_2}$ — •Ines Wagner-Drebenstedt, Jürgen Plenge, Markus Kurth, Janis Berkemeyer und Eckart Rühl — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Es werden Experimente vorgestellt, in denen die ultraschnelle photoinduzierte Dynamik von Rydberg-Zuständen des Kohlenstoffdisulfids (CS_2) mit Hilfe der zeitaufgelösten Photoelektronenspektroskopie untersucht wurde. In Anregungs-Nachweis Experimenten erfolgte die primäre Ein-Photonen-Anregung der Rydberg-Zustände $4p^1\Pi_u$ bzw. $4p^3\Pi_u$ durch die 5. Harmonische eines Titan-Saphir Femtosekunden-Lasersystems, bei einer Photonenenergie von 7,75 eV. Die angeregten Zustände wurden nachfolgend entweder durch 800 nm oder durch 400 nm Femtosekunden-Laserstrahlung ionisiert. Aus den zeitabhängigen Photoelektronenausbeuten wurden für die Rydberg-Zustände $4p^1\Pi_u$ und $4p^3\Pi_u$ Lebensdauern von 632 ± 22 fs bzw. 2225 ± 125 fs ermittelt, die auf einen prädissoziativen Zerfall der primär angeregten Zustände hinweisen. Darüber hinaus zeigen die zeitaufgelösten Elektronenausbeuten die Dynamik von Schwingungswellenpaketen, die auf die kohärente Anregung der symmetrischer Streckschwingung und der Biegeschwingung im $4p^1\Pi_u$-Zustand bzw. der antisymmetrischen Streckschwingung und der Biegeschwingung im $4p^3\Pi_u$-Zustand zurückgeführt werden.

MO 12.10 Wed 12:45 TOE 317

Ultrafast time-resolved photoelectron spectroscopy of benzene — •Peter Lang[1,2], Christian Homann[1], Igor Pugliesi[1], Reinhard Kienberger[2], and Eberhard Riedle[1] — [1]Dep. for biomolecular optics, LMU Munich — [2]Dep. for physics, TU Munich

Time resolved photoelectron spectroscopy is a versatile tool for the investigation of ultrafast dynamics in optically dark regions of the molecular potential energy surface. We developed a novel pump-probe-setup, which consists of a magnetic bottle and two tunable laser pulses with pulse durations better than 30fs. The pump pulse covers a range of 240 - 400 nm and is used to excite the molecule. The temporally delayed probe pulse with 200 - 240 nm ionizes the excited molecules. This deep-UV probe pulse samples a large range of the electron kinetic energy spectrum up to 3 eV. The tunability allows to minimize the contribution of electronic excitations by the probe pulse alone.

Since the energy distribution in the excited molecule changes through electronic and vibrational and electronic relaxation, the kinetic energy of the electrons changes as a function of pump-probe delay. While the magnetic bottle is used to measure the electron kinetic energy, we can also record ion mass spectra to detect possible fragmentation products.

With a pump-probe cross correlation of better than 40 fs we are able to directly observe the ultrafast S2-S1 relaxation of benzene. The measurements show a shift in the electron spectra towards smaller kinetic energies as the molecule relaxes into the S1-state. This process occurs within less than 100 fs.