MO 12: Femtosecond Spectroscopy III

Time: Tuesday 14:00–16:00 Location: F 102

Invited Talk MO 12.1 Tue 14:00 F 102

Strong Field Molecular Ionization — •Thomas Weinacht — Stony Brook, University, Stony Brook, NY

Strong Field Molecular Ionization has become an important cornerstone of ultrafast spectroscopy. It is the first step in High Harmonic Generation and following attosecond electronic dynamics. It has also been used as a probe of molecular structure. This talk will focus on strong field molecular ionization as a probe of dynamics and structure, highlighting experiments that aim to deepen our understanding of the ionization process itself as well as experiments that make use of ionization as a probe of excited state molecular dynamics.

MO 12.2 Tue 14:30 F 102

Laser photofragmentation and ultrafast time-resolved dynamics of mass-selected ionic species — •Christoph Riehn, Yevgeniy Nosenko, Dimitri Imanbaew, and Sebastian Kruppa — Fachbereich Chemie,TU Kaiserslautern, D-67663 Kaiserslautern, Erwin-Schroedinger-Str. 52

The influence of metal-metal or metal-ligand interaction on elementary processes (electronic coupling; energy, charge transfer and fragmentation dynamics) of mass-selected, isolated metal-ligand species is studied at a 50 fs-100 ps time scale. The newly designed experimental setup consists of a kHz 50 fs-amplified Ti:Sa-laser system equipped with two optical parametrical generator units and an electrospray ion trap mass spectrometer. The time-resolved measurements are based on pump-probe transient photofragmentation.[1] Our first results for the transient photofragmentation of protonated tryptophan at various pump-probe wavelengths will be discussed [2] and compared to the tryptophan-Ag+ complex, where charge transfer plays an important role. Finally, we present time-resolved measurements on a dianionic Diplatinum-complex [Pt2(P2O5H2)4H2]2- and its silver-containing derivative [Pt2(P2O5H2)4AgH]2-. It shows ultrafast electronic dynamics in the gas phase detected via the parallel channels of electron detachment and photofragmentation.

References: [1] D. Nölting, T. Schultz, I.V. Hertel, R. Weinkauf, Phys. Chem. Chem. Phys. 2006, 8, 5247- 5254. [2] H. Kang, C. Dedonder-Lardeux, C. Jouvet, G. Gregoire, C. Desfrancois, J.-P. Schermann, M. Barat, J. A. Fayeton, J. Phys. Chem. A 2005, 109, 2417-2420.

MO 12.3 Tue 14:45 F 102

Ultrafast photofragment ion spectroscopy of the Wolff rearrangement in 5-diazo Meldrum's acid in the gas phase — Andreas Steinbacher, •Sebastian Roeding, Tobias Brixner, and Patrick Nuernberger — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We investigate the multisequential photochemistry of 5-diazo Meldrum's acid (DMA), a photoactive compound used in lithography, by femtosecond photofragment ion spectroscopy in the gas phase. Former studies [1,2] in solution revealed an ultrafast intramolecular Wolff rearrangement to a ketene after UV excitation, followed by subsequent reactions with a solvent molecule. In this gas phase study, the absence of interactions and reactions with solvent molecules allows us to focus on the photochemistry of the ketene intermediate. Besides direct fragmentation of this intermediate to acetone and carbon monoxide, we further find experimental indications that a second Wolff rearrangement occurs, as was conjectured earlier for this molecule [3] from photofragment analysis.

[1] P. Rudolf, J. Buback, J. Aulbach, P. Nuernberger, and T. Brixner, JACS 2010, 132, 15213-15222

[2] G. Burdzinski, J. Réhault, J. Wang, and M. S. Platz, J. Phys. Chem. A 2008, 112, 10108-10112

[3] S. L. Kammula, H. L. Tracer, P. B. Shevlin, and M. Jones, J. Org. Chem. 1977, 42, 2931

Invited Talk MO 12.4 Tue 15:00 F 102

Photoelectron angular distributions of chiral molecules from multi-photon ionization — •Matthias Wollenhaupt, Christian Lux, Vanessa Brandenstein, Cristian Sarpe, and Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) [1] was previously investigated on small chiral molecules using synchrotron radiation. The observed asymmetries in the PECD arise in forward/backward direction with respect to the light propagation. Recently, we have demonstrated a circular dichroism effect in the plus/minus ten percent regime derived from images of photoelectron angular distributions resulting from 2+1 REMPI of randomly oriented chiral molecules in the gas phase, where Camphor and Fenchone were chosen as prototypes [2]. The PECD was also observed in the Above Threshold Ionization (ATI) photoelectrons. Currently, we study nuclear and electron dynamics on the intermediate resonance with the help coherent control techniques [3]. In addition, we have developed a tomographic reconstruction method to directly measure three-dimensional photoelectron angular distributions resulting from REMPI in a Velocity Map Imaging (VMI) set-up [4]. On atoms we have demonstrated the creation of designer electron wave packets using polarization shaped laser pulses.

[1] I. Powis, in Adv. Chem. Phys. 138, 267 (2008).

[2] C. Lux et al., Angew. Chem. Int. Ed. 51, 5001 (2012).

[3] M. Wollenhaupt and T. Baumert, Faraday Discuss. 153, 9, (2011).

[4] M. Wollenhaupt et al., Appl. Phys. B 95, 647, (2009).

MO 12.5 Tue 15:30 F 102

Fragmentation und Coulomb Explosion Imaging isotopenchiraler Moleküle — •Martin Pitzer, Markus S. Schöffler, Maksim Kunitski, Allan S. Johnson, Till Jahnke, Lothar Ph. H. Schmidt, Horst Schmidt-Böcking und Reinhard Dörner — Institut für Kernphysik, Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, 60438 Frankfurt am Main

Die Untersuchung chiraler Moleküle ist von großem Interesse in der Biochemie und Pharmazeutik, aber auch bei der Erforschung fundamentaler Symmetrieeigenschaften der Naturgesetze, z.B. der Paritätsverletzung. Bisherige experimentelle Methoden beschränken sich jedoch auf die Messung von über viele Moleküle gemittelten Größen. Mit der ColTRIMS-Methode (Cold Target Recoil Ion Momentum Spectroscopy) ist es möglich, die Impulse der Elektronen und Ionen aus der Fragmentation eines Einzelmoleküls zu rekonstruieren, und diese vektoriellen Größen zueinander in Beziehung zu setzen. Dies eröffnet faszinierende neue Möglichkeiten zur Untersuchung chiraler Systeme, wie die Darstellung von Winkelverteilungen im Molekülsystem oder die Definition abgeleiteter Vektorgrößen.

In einem ersten Schritt wurde das isotopenchirale Molekül $CHCl_2Br$ mit Hilfe von fs-Laserpulsen ionisiert und die resultierenden Ionenfragmente orts- und zeitaufgelöst detektiert. Für verschiedene Zerfallskanäle konnten die Fragmente identifiziert und die Impulse bestimmt werden, insbesondere für die vollständige Fragmentation in 5 Ionen. Zudem wurde mit Aceton ein organisches Molekül höherer Komplexität untersucht und die Fragmentation in bis zu 9 Ionen demonstriert.

MO 12.6 Tue 15:45 F 102

Photoelectron Circular Dichroism of Chiral Molecules from Multi Photon Ionization with Femtosecond Laser Pulses: Intensity and Ellipticity studies — •Christian Lux, Vanessa Brandenstein, Jens Köhler, Cristian Sarpe, Matthias Wollenhaupt, and Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) shows asymmetries in the electron emission from chiral enantiomers relative to the light propagation direction and was so far investigated using synchrotron radiation [1]. The magnitude of PECD is several orders larger than typically chirooptical asymmetries. Resonance Enhanced Multi-Photon Ionization (REMPI) in mass spectrometry of chiral molecules using laser pulses results in strong asymmetries in the absorption of circularly polarized light [2,3]. We have demonstrated that PECD on randomly oriented chiral enantiomers is accessible via a 2+1 REMPI using femtosecond laser pulses, containing highly structured asymmetries in the ± 10% regime [4]. In this contribution we present our recent findings on the bicyclic ketones Camphor, Norcamphor and Fenchone. On variation of the laser intensity, we observe dissociative ionization. However, the PECD can be unambiguously attributed to direct ionization of the parent ion. Ellipticity studies show the robustness of the PECD effect.

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

[2] C. Logé, U. Boesl, Chem. Phys. Chem. **12**, 1940-1947 (2011)

[3] P. Horsch, G. Urbasch, K.-M. Weitzel, Chirality **24**, 684-690 (2012)

[4] C. Lux et al., Angew. Chem. Int. Ed. **51**, 5001-5005 (2012)