

MO 3: Photoelectron Spectroscopy

Time: Monday 10:30–12:30

Location: PA 2.150

Invited Talk

MO 3.1 Mon 10:30 PA 2.150

Electronic structure and relaxation of solvated organic molecules studied by time-resolved photoelectron spectroscopy — JOHAN HUMMERT, GEERT REITSMA, NICOLA MAYER, EVGENII IKONNIKOV, MARTIN ECKSTEIN, and OLEG KORNILOV — Max Born Institute, Berlin, Germany

Photoactive processes play a role in many biological systems from human vision to light harvesting. Electronic relaxation and structural rearrangements following photon absorption often strongly depend on the chromophore environment. These dynamics are extensively studied by all-optical techniques, but the tools of time-resolved photoelectron spectroscopy (TRPES), which brought many insights in gas phase and in solid state physics, have not been applied until recently. In this contribution we demonstrate TRPES of organic molecules in aqueous solutions combining monochromatized femtosecond XUV pulses [1] and the microliquid jet technology. We analyze electronic structure of several organic molecules and follow relaxation dynamics of one of them, Quinoline Yellow. Quinoline Yellow in a non-polar aprotic solvent was recently suggested to undergo an excited state proton transfer (ESPT) from a nitrogen to an oxygen atom [2]. Relaxation timescales obtained in our experiment are consistent with this proposal, but the process seems to be faster in water. Additionally, our results indicate an ultrafast solvent rearrangement following a significant change of molecular dipole upon electronic excitation. [1] M. Eckstein et al, Phys. Rev. Lett. 116, 163003 (2016) [2] G. R. Han et al, Sci. Reports, 7, 3863 (2017)

MO 3.2 Mon 11:00 PA 2.150

A ps time-resolved photoelectron imaging study on the photophysics of Acenaphthylene — MARCO FLOCK, MAX HERBERT, and INGO FISCHER — Institute of Physical and Theoretical Chemistry, Julius Maximilians University of Wuerzburg, Germany

Acenaphthylene is a member of the chemical group of polycyclic aromatic hydrocarbons (PAHs). PAHs are a toxic and cancerogen species and are emitted to the environment mainly through incomplete combustion processes. Thus, they are supposed to significantly increase the risk of human cancer diseases. Beside their toxicology, PAHs show interesting photophysical properties and are promising building blocks for devices like semiconductors or solar cells. In our studies, we investigated the excited state dynamics of the S1 and S2 state of Acenaphthylene. Time-resolved TOF photoionization and photoelectron imaging experiments showed an IC transition from the S1 state to the ground state with decreasing lifetimes from 480 ps at the S1 origin to 100 ps at a vibronic excess energy of 2700 cm⁻¹. In further experiments, a monoexponential decay after excitation of the S2 state was detected. This can be explained by a very fast IC transition to the high vibronically excited S1 state, followed by another IC to the electronic ground state. The time constant of this second process further decreases to a value of around 55 ps. Besides, time resolved photoelectron images show a constant signal offset at long delay times, which indicates a competing ISC transition to the triplet manifold after S2 excitation.

MO 3.3 Mon 11:15 PA 2.150

Multi-state Photoelectron Circular Dichroism in Femtosecond Multiphoton Ionization — ALEXANDER KASTNER¹, TOM RING¹, ROXANA SAVULEA¹, BASTIAN C. KRÜGER², G. BARRATT PARK², TIM SCHÄFER², ARNE SENFTLEBEN¹, and THOMAS BAUMERT¹ — ¹Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — ²Institut für Physikalische Chemie, Georg-August-Universität Göttingen, D-37077 Göttingen, 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]. Due to the multi-photon ionization, we observed highly structured asymmetries with a magnitude in the range of $\pm 10\%$ on bicyclic Ketones [3, 4]. By scanning the laser excitation wavelength, up to three electronically distinct resonances can be simultaneously populated. The intermediate state and the excitation wavelength define the photoelectron energy. We report on the dependence of magnitude and sign of PECD on photoelectron energy [5].

- [1] I. Powis, 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)
- [5] A. Kastner et al., J. Chem. Phys. 147, 013926, (2017)

MO 3.4 Mon 11:30 PA 2.150

Photoelectron spectroscopy of organic molecules in protic and aprotic solvents — EVGENII IKONNIKOV, JOHAN HUMMERT, GEERT REITSMA, and OLEG KORNILOV — Max Born Institute, Berlin, Germany

The environment of the molecules can cause changes in relaxation dynamics especially in protic solvents, where additional H bonds exist, which cannot be observed in vacuum. Here we use photoelectron spectroscopy in combination with a microliquid jet to study molecules in solution. The method allows us to measure binding energies, energies of excited states and lifetimes using a pump-probe technique. For these experiments we recently developed experimental beamline using HHG [1] to measure time-resolved photoelectron spectra of solvated molecules in water. In this report we present the first results for several solvents and solvated molecules using this technique. Specifically we extend our experiments to protic and non-protic solvents. In time-resolved experiments we use short XUV pulse (30 fs) as a probe pulse and visible 400 nm (30 fs) pulse as a pump-pulse. [1] M. Eckstein et al, Phys. Rev. Lett. 116, 163003 2016

MO 3.5 Mon 11:45 PA 2.150

Time-resolved photoelectron spectroscopy of deuterated Ethylene in the VUV with interferometric contrast — OLIVER SCHEPP¹, ARNE BAUMANN¹, MAREK WIELAND^{1,2,3}, and MARKUS DRESCHER^{1,2,3} — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg — ²The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg — ³Centre for Free-Electron-Laser Science, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg

Ethylene and its deuterated isotopologues are prototypical molecules for studying non-adiabatic dynamics in small organic systems. Irradiation in the vacuum ultraviolet spectral range gives access to $\pi \rightarrow \pi^*$ excitation, followed by its ultrafast relaxation to the ground state through two conical intersections, including twisted-pyramidalization and proton migration.

Here we present a scheme using femtosecond vacuum ultraviolet pulses for both pump and probe in a co-propagating geometry enabling interferometric resolution for the pump probe signal [1]. The delay-dependent photoelectron spectra gives access to the ultrafast wavepacket dynamics on different time scales observed for different electron energies. Further, we observe a coherent beating pattern in the pump-probe signal which is attributed to the combined stretch and torsional modes of the C-C double bond.

- [1] T. Gebert, D. Rompotis, M. Wieland, F. Karimi, A. Azima, M. Drescher, New J. Phys. 16 0170347 (2014).

MO 3.6 Mon 12:00 PA 2.150

Photoelectron Spectroscopy of Triplet Pentadiynylidene and Methylpentadiynylidene — ENGELBERT REUSCH¹, DOMENIK SCHLEIER¹, PATRICK HEMBERGER², and INGO FISCHER¹ — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074, Germany — ²Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institut (PSI), CH-5232 Villigen, Switzerland

Highly unsaturated and carbon-rich chain molecules like Pentadiynylidene (HC5H) and Methylpentadiynylidene (MeC5H) occur as unstable intermediates in harsh chemical environments. They are well studied by various techniques like matrix isolated IR, EPR and UV/VIS spectroscopy.[1] Nevertheless, Threshold Photoelectron Spectra (TPES) of HC5H and MeC5H didn't exist. To obtain first insights we applied imaging Photoelectron Photoion Coincidence Spectroscopy in this study, which is capable to supply mass selective TPES. 1-Diazopenta-2,4-diyne and 1-Diazo-hexa-2,4-diyne were selected as excellent precursors generating Triplet Pentadiynylidene and Methylpentadiynylidene. Ensuing the corresponding carbenes were produced by

flash pyrolysis, stabilized in the gas phase and photoionized by tunable vacuum ultraviolet synchrotron radiation. This presentation will offer first results in the Photoelectron Spectroscopy of Pentadiynylidene and Methylpentadiynylidene, executed at the Swiss Light Source (SLS) for synchrotron radiation. [1] Bowling, N. P.; Halter, R. J.; Hodges, J. A.; Seburg, R. A.; Thomas, P. S.; Simmons, C. S.; Stanton, J. F.; McMahan, R. J., *J. Am. Chem. Soc.*, 128, 3291-3302 (2006).

MO 3.7 Mon 12:15 PA 2.150

Energy resolved Auger spectra of thymine after excitation with UV light — •JAN METJE¹, THOMAS J.A. WOLF², and MARKUS GÜHR¹ — ¹University of Potsdam, Potsdam, Germany — ²Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, USA

Energy conversion in UV-excited molecules often involves coupled elec-

tronic and nuclear dynamics not fulfilling the Born-Oppenheimer approximation. Their experimental investigation is complicated by the existence of dark $n\pi^*$ states if the molecule contains heteroatoms. One such chromophore is the model system thymine.

It has been studied with a variety of time-resolved methods including non-resonant Auger and NEXAFS spectroscopy [1,2]. From the former study, it was concluded that the relaxation of UV-excited thymine involves a $\pi/\pi^* \rightarrow n\pi^*$ transition. The absorption of this $n\pi^*$ state was observed in integrated Auger spectra of the latter study and determined to happen on a (60 ± 30) fs timescale.

We show energy resolved Auger spectra of thymine at resonant absorption lines in NEXAFS spectra after UV excitation and discuss their sensitivity on the molecular relaxation process.

Full author list: see [2] and Jan Metje.

[1] McFarland et.al., *Nature Comm.* **5**:4235, 2014

[2] Wolf et.al., *Nature Comm.* **8**:29, 2017