

MO 17: Electronic Spectroscopy 2

Time: Thursday 14:30–16:00

Location: f102

MO 17.1 Thu 14:30 f102

Molecular-Frame Photoelectron Imaging of Controlled Complex Molecules — ●JOSS WIESE¹, SEBASTIAN TRIPPEL¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²The Hamburg Center for Ultrafast Imaging, Hamburg — ³Department of Physics, University of Hamburg

Since chemical function arises from the interplay amongst valence electrons, a view at the evolution of the highest occupied molecular orbitals (HOMOs) during a chemical reaction promises direct insight into the fundamentals of chemistry. Therefore, we employ tomographic photoelectron imaging of spatially controlled complex molecules strong-field ionised by intense near-infrared laser pulses [1]. Reconstructed static three-dimensional photoelectron distributions in molecular-frame velocity space of indole and its water complex will be presented. These allow for the observation of the molecules' electron density distributions, photoelectron kinetic energies, and off-molecular-plane emission angles in 3D. The experimentally retrieved observables are discussed employing an extended strong-field approximation model. Those three observables provide a close glimpse at the laser-distorted HOMO potential surfaces of the investigated molecules in the gas phase and yield access to their changes in polarisability and dipole moment upon ionisation. Furthermore, the direct comparison of indole and its water complex allows inspection of the nature of hydrogen bonding in heteroaromatic biomolecules.

[1] Maurer, Dimitrovski, Christensen, Madsen, Stapelfeldt, *PRL* **109**, 123001 (2012)

MO 17.2 Thu 14:45 f102

Collective excitations and their impact on plasmon-induced double photoemission from fullerenes — MICHAEL SCHÜLER¹, YAROSLAV PAVLYUKH¹, PAOLA BOLOGNESI², LORENZO AVALDI², and ●JAMAL BERAKDAR¹ — ¹Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany — ²CNR-ISM, Area della Ricerca di Roma 1, CP10, 00016 Monterotondo Scalo, Italy

The correlated release of an electron pair from a sample upon absorbing one photon, called double photoemission (DPE), is a process that is particularly sensitive to the effective electron-electron interaction. As a prototypical example we consider the C₆₀ molecule. We analyse its strongly pronounced collective many-body excitations (plasmons) using ab initio calculations based on the time-dependent density-functional theory (TDDFT). Utilizing the nonnegative matrix factorization method, the individual plasmon modes are isolated and characterized by their multipolar and spatial distribution of the associated charge-density oscillations. This allows to construct a new model for the density-density response function and the effective electron-electron interaction that accurately describes typical experiments such as electron-energy loss spectroscopy (EELS). Using our model parameterization of screened interaction and further ab initio calculations, we compute the electron-pair coincidence spectrum of C₆₀. Both theory and experiment underpin the new features arising from the dynamically screened interaction mediating the effective electron-electron interaction and thus endorse DPE as a powerful tool for tracing electron pair correlations in complex many-body systems.

MO 17.3 Thu 15:00 f102

Multimodal Time-Resolved Spectroscopy of Vibrational Coherence and Population Dynamics in the Excited State — ●TAKESHI MIKI, MARCUS MOTZKUS, and TIAGO BUCKUP — Physikalisches-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The interpretation of dynamics in the excited states of molecules often challenges time-resolved spectroscopy in particular due to spectrally overlapping contributions as well as ultrafast optical signals. Multimodal Time-Resolved Spectroscopy combines multiple time-resolved signals to disentangle and map complex molecular dynamics. In this work we exploit two different time-resolved spectroscopies, transient absorption (TA) spectroscopy and pump-degenerate four wave mixing (pump-DFWM) spectroscopy, to map the interplay between population and vibrational coherence dynamics. An algorithm is developed to globally fit the whole spectrally resolved data of both methods. A kinetic model is developed via global target analysis of the TA data, which is further refined by exploiting the very sensitive homodyne sig-

nal of pump-DFWM spectroscopy. This way, time decay constants of electronic states, frequency and phase of vibrational molecular modes, and transition dipole moments of excited state transitions can be obtained under the assumption of a unified molecular model. This is applied (i) to disentangle the vibrationally modulated from the not vibrationally modulated stimulated emission and (ii) to determine specific vibrational frequencies and their origin during the deactivation of electronic states. The method is applied to prototype organic molecules.

MO 17.4 Thu 15:15 f102

Investigations on the isolated diphenyl ether-methanol complex by combined IR/UV spectroscopy in the electronically excited and the ionic state — ●DOMINIC BERNHARD¹, ANKE STAMM¹, FABIAN DIETRICH¹, CHRISTOF HOLZER², WILLEM KLOPPER², and MARKUS GERHARDS¹ — ¹Fachbereich Chemie, TU Kaiserslautern — ²Institut für Physikalische Chemie, KIT

Dispersion interactions are ubiquitous regarding intermolecular interactions. Their relative contributions strongly vary depending on the investigated system and the theoretical prediction of these contributions is challenging. Diphenyl ether represents a system with competing docking sites for methanol: the ether oxygen atom as a well-known hydrogen bond acceptor and the two phenyl rings as dispersion energy donors can lead to π binding. Interestingly, both calculated binding motifs are predicted to be almost equally stable, requiring an experimental verification. Therefore, we investigated the diphenyl ether-methanol complex in molecular beam experiments using IR/UV and IR/IR/UV spectroscopy in the electronic ground state (S₀), the electronically excited state (S₁) and the ionic ground state (D₀). In the S₀ state the OH... π type structure is dominating, whereas the slightly less stable OH...O isomer is far less abundant (cooperation with the groups of Prof. Martin Suhm, University of Göttingen and PD Melanie Schnell, MPSD Hamburg). This talk will be focussed on the results for the S₁ and D₀ state. In the S₁ state different isomers are discussed and compared with theory. A structural rearrangement takes place in the D₀ state due to electrostatic effects.

MO 17.5 Thu 15:30 f102

A Flatjet System for Soft X-Ray Spectroscopy in the Liquid Phase — ●MARIA EKIMOVA¹, WILSON QUEVEDO², MANFRED FAUBEL³, PHILIPPE WERNET², and ERIK NIBBERING¹ — ¹Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Berlin, Germany — ²Institute for Methods and Instrumentation for Synchrotron Radiation Research, HZB, Berlin, Germany — ³Max Planck Institute for Dynamics and Self-Organization, Goettingen, Germany

Recent progress in soft-X-ray absorption spectroscopy (XAS) has led to new insights into the local molecular interactions in liquid water, alcohols and in solutions. The methods used to measure XAS typically involve either standing sample cells with silicon nitride (Si₃N₄) membranes or single liquid jets. Signal contribution of the Si₃N₄ membrane, or possible radiation damage may complicate the sample cell approach. Single liquid jets on the other hand have limited diameter, preventing a proper XAS measurement in transmission mode. Here, we present [1] a *free-windows* flatjet system as a new approach to perform solution-phase soft X-ray spectroscopy directly in transmission mode. The collision of two single jets with a diameter of 50 μ m under an impact angle of 48° leads to double sheet formation, of which the first sheet is 6 mm long, 1 mm wide and with a thickness of 1,4-3 μ m. We demonstrate the feasibility of N and O K-edge transmission XAS of salt solutions. Our results pave the way of using liquid flatjets both in steady-state and ultrafast soft X-ray spectroscopy.

References:

[1] M. Ekimova et al., *Struct.Dyn.* **2**, 054301 (2015)

MO 17.6 Thu 15:45 f102

Laser-induced acoustic desorption of large molecules via tape-drive method — ●ZHIPENG HUANG^{1,3}, DANIEL A. HORKE^{1,2}, MATTHIAS SCHUST¹, TIM OSSENBRÜGGEN¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²Center for Ultrafast Imaging, University of Hamburg — ³Department of Physics, University of Hamburg

By dispersing molecular beams with strong electric fields, we can routinely produce pure samples of individual conformers or clusters ac-

ording to their quantum state. Selected molecules can be further controlled using alignment and orientation by laser and static electric fields [1]. We are currently working towards extending these techniques to much large molecules and systems.

Laser-induced acoustic desorption (LIAD) is a promising technique for gentle and efficient preparation of large intact neutral molecules in the gas-phase [2]. Here we demonstrate our newly set-up LIAD source, designed for prolonged measurement times through automatic sample replenishment. Molecules are sprayed onto a long 10 μm tanta-

lum foil band that is irradiated from the backside by a third harmonic Nd:YAG laser (355 nm). The induced shockwave travels through the foil and desorbs molecules from the frontside of the foil. We present results and characterizations of the source, and discuss its potential for applications in x-ray or electron diffraction imaging.

[1] Y.P. Chang, D. A. Horke, S. Trippel and J. Küpper, *Int. Rev. Phys Chem.* **34**, 557 (2015)

[2] B. Linder and U. Seydel, *Anal. Chem.* **57**, 895 (1985)