

## MO 17: Experimental Techniques

Time: Friday 11:00–13:00

Location: N 6

## Invited Talk

MO 17.1 Fri 11:00 N 6

**Molecular-Frame Photoelectron Imaging of Controlled Complex Molecules** — ●JOSS WIESE<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg — <sup>2</sup>The Hamburg Center for Ultrafast Imaging, Hamburg — <sup>3</sup>Department 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. We employ tomographic photoelectron imaging [1] of spatially controlled ensembles of indole and its 1:1 water complex strong-field ionised by intense near-infrared laser pulses. Reconstructed static three-dimensional photoelectron distributions in molecular-frame velocity space 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 Fri 11:30 N 6

**New pump-probe ITOF setup to unravel ultra-fast photo-conversion processes** — ●MARIO NIEBUHR, DENNIS MAYER, TOM NEUMANN, AXEL HEUER, and MARKUS GÜHR — Institute for Physics and Astronomy, Uni Potsdam, Germany

Ultra-fast pump-probe spectroscopy of isolated molecules presents an important step towards understanding photo conversion processes and provides benchmark data for high-level ab-initio calculations. We are especially interested in photoisomerization systems such as azobenzene, and molecules, such as nucleobases, that are able to withstand energetic UV irradiation through very fast, non-ionizing and non-dissociating relaxation channels.

Our new setup utilizes time-of-flight mass spectroscopy to obtain delay dependent signals from excited state intramolecular conversion processes with femtosecond time resolution. We use a commercial 100 kHz Yb:KGW system and it's harmonics for pumping as well as probing. As the pulses for Yb based lasers are typically in the several 100 fs range, noncollinear parametric amplifiers (NOPAs) and fiber based spectral broadening are employed to access the sub hundred fs regime. First data of delay-dependent ion fragmentation yields will be presented.

MO 17.3 Fri 11:45 N 6

**Broadband 7-fs 2D electronic spectroscopy by hollow-core fiber compression** — ●XIAONAN MA, JAKUB DOSTÁL, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent two-dimensional electronic spectroscopy (2DES) is a powerful technique for resolving excited-state dynamics within coupled systems. To date, 2DES is mainly limited by laser bandwidth and peak-shape distortion (*e.g.* directional filtering) [1]. In this work, we combine a sub-7-fs supercontinuum generated in Ar-filled hollow-core fiber (HCF) with a diffractive-optic-based 2DES spectrometer for broadband 2DES measurement (500-700 nm) and reducing peak-shape distortion to a minimum [2].

We demonstrated the technique with cresyl-violet in ethanol. Measuring transient absorption in the same setup allow us to phase the 2DES data. The resulting peak-shape and quantum beating behaviour (585 and 2820  $cm^{-1}$ ) agree with a previous report [3]. We note that with sub-7-fs temporal resolution, our setup has the potential to observe extremely fast quantum beating (up to 3500  $cm^{-1}$ ), which is especially suited to investigate multi-chromophore systems with strong excitonic coupling. Meanwhile, this technique can be extended to even broader wavelength range (*i.e.* > 1 octave) or other regimes (*i.e.* UV and NIR).

[1] M. K. Yezzbacher *et al.*, *J. Chem. Phys.* **126**, 044511 (2007).

[2] X. Ma *et al.*, *Opt. Express* **24**, 20781 (2016).

[3] L. A. Bizimana *et al.*, *J. Chem. Phys.* **143**, 164203 (2015).

MO 17.4 Fri 12:00 N 6

**Development of Cavity Ring-Down Spectroscopy for Carbon Isotope Analysis of Biomedical Samples** — ●VOLKER SONNENSCHNEIN<sup>1</sup>, RYOHEI TERABAYASHI<sup>1</sup>, HIDEKI TOMITA<sup>1</sup>, NORIYOSHI HAYASHI<sup>1</sup>, SHUSUKE KATO<sup>1</sup>, LEI JIN<sup>1</sup>, MASAHIKO YAMANAKA<sup>1</sup>, NORIHIKO NISHIZAWA<sup>1</sup>, ATSUSHI SATO<sup>2</sup>, KOHEI NOZAWA<sup>2</sup>, KENTA HASHIZUME<sup>2</sup>, TOSHINARI OH-HARA<sup>2</sup>, and TETSUO IGUCHI<sup>1</sup> — <sup>1</sup>Graduate School of Quantum Engineering, Dep. of Engineering, Nagoya University, Nagoya, Japan. — <sup>2</sup>ADME and Tox. Research Institute, Sekisui Medical, Tokai, Ibaraki, Japan

High sensitivity techniques such as Accelerator Mass spectrometry are commonly used for detection of the radioisotope <sup>14</sup>C. In the environment, its abundance is typically at the ppt level, however in medical samples, where it is used as tracer isotope to study the metabolism of subjects or other biological processes, the abundance can be significantly higher. Detection may then be performed by application of optical methods such as Cavity Ring-Down Spectroscopy (CRDS), thus providing a more compact and inexpensive solution as well as possibilities for in-field measurements.

An overview and status of our current system for CRDS of <sup>14</sup>CO<sub>2</sub> in the Mid-IR wavelength range will be given. The optical cavity is directly coupled to a CHNS elemental analyzer, allowing quick sample analysis. Thermo-electric cooling is applied to suppress interference by absorption of other close-lying molecular transitions. Remaining contaminants in biomedical samples are analyzed and the sensitivity and linearity of the <sup>14</sup>C determination are estimated.

MO 17.5 Fri 12:15 N 6

**Signal reversing cavity-based polarimetry: Measuring Chirality and Atomic Parity Nonconservation** — ●ALEXANDROS K. SPILIOTIS<sup>1,2</sup>, DIMITRIOS SOFIKITIS<sup>1</sup>, GEORGIOS E. KATSOPRINAKIS<sup>1</sup>, and T. PETER RAKITZIS<sup>1</sup> — <sup>1</sup>Institute of Electronic Structure and Laser, Foundation for Research and Technology - Hellas, 71110 Heraklion, Greece — <sup>2</sup>Department of Physics, University of Crete, 71003 Heraklion, Greece

Chirality is a fundamental property of life. Thus, chiral sensing and analysis is of fundamental importance in a number of scientific fields, ranging from pharmacology to fundamental physics and chemistry. The main constraint in the measurement of chiral signals is that they are typically very small and are thus limited by spurious birefringence and poor background subtraction procedures. Recently, our group has introduced a new cavity-based technique, which aims to overcome all these problems. The technique uses an optical cavity, which enhances the Optical Rotation (OR) signals by the number of cavity passes (typically ~1000). A number of signal reversals are incorporated in this method, which allow absolute measurements of chiral signals, without the need for background subtraction; the reversals suppress the spurious background birefringence, thus allowing the measurement of relatively small OR. This cavity-based setup has been proposed as a low-energy, table-top test of the Standard Model. It can be used for the detection of Atomic Parity nonconservation (PNC), to precisely measure the cavity-enhanced parity-nonconserving OR of molecular transitions, in molecules such as Xe and Hg and I<sub>2</sub>.

MO 17.6 Fri 12:30 N 6

**Collinear rapid-scan two-dimensional spectroscopy via fluorescence detection with shot-to-shot phase cycling** — ●SIMON DRAEGER, SEBASTIAN ROEDING, JAKUB DOSTÁL, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present pulse-shaper-assisted coherent two-dimensional (2D) electronic spectroscopy in liquids using fluorescence detection. A customized pulse shaper facilitates shot-to-shot modulation at 1 kHz and is employed for rapid scanning over all time delays. Phase cycling is used to extract the coherent information from the incoherent fluorescence signal. This enables us to obtain a full 2D spectrum with different nonlinear contributions in approximately 6 s measurement time (plus further averaging if needed). The method is applicable to various chemical systems. We employ cresyl violet in ethanol as a benchmark

system.

MO 17.7 Fri 12:45 N 6

**Time-dependent analysis of the mixed-field orientation of molecules without rotational symmetry** — •LINDA V. THESING<sup>1</sup>, ROSARIO GONZÁLEZ-FÉREZ<sup>2</sup>, and JOCHEN KÜPPER<sup>1,3,4</sup> —

<sup>1</sup>Center for Free-Electron Laser Science, DESY — <sup>2</sup>Instituto Carlos I, Universidad de Granada — <sup>3</sup>The Hamburg Center for Ultrafast Imaging, University of Hamburg — <sup>4</sup>Department of Physics, University of Hamburg

We present a time-dependent study of the rotational dynamics of molecules without rotational symmetry and compute the 1D and 3D

orientation in combined ac and dc electric fields. For a weak dc field, our results for the 1D orientation of a thermal ensemble of 6-chloropyridazine-3-carbonitrile (CPC) molecules are in good agreement with experimental observations for a state selected sample [1]. For an elliptically polarized laser, our theoretical results additionally show that the molecules are 3D oriented. If the dc field strength is increased, the 3D orientation is enhanced for certain angles between the ac and dc fields. Analyzing the field-dressed dynamics as the laser is turned on, we find highly non-adiabatic effects due to the complex energy level structure of the CPC molecule, and investigate their impact on the mixed-field orientation.

[1] Hansen et al., *J. Chem. Phys.* **139**, 234313 (2013)