

## MO 15: Femtosecond Spectroscopy 3

Time: Thursday 11:00–13:15

Location: f102

## Invited Talk

MO 15.1 Thu 11:00 f102

**Imaging of an autoionizing resonance using time-, energy- and angular-resolved photoelectron spectroscopy.** — MARTIN ECKSTEIN<sup>1</sup>, CHUNG-HSIN YANG<sup>1</sup>, FABIO FRASSETTO<sup>2</sup>, LUCA POLETTO<sup>2</sup>, GIUSEPPE SANSONE<sup>3</sup>, MARC J. J. VRAKING<sup>1</sup>, and OLEG KORNILOV<sup>1</sup> — <sup>1</sup>Max-Born-Institute, Berlin, Germany — <sup>2</sup>CNR-IFN, Padova, Italy — <sup>3</sup>Politecnico, Milan, Italy

One of the prominent examples of multielectron dynamics is the atomic and molecular autoionization - emission of an electron from an electronically excited system. Such processes typically happen on time-scales of few tens of femtoseconds and requires time-resolved methods with excellent resolution. Here we investigate autoionizing Rydberg states of molecular nitrogen using time-, energy- and angular-resolved photoelectron spectroscopy employing a recently constructed time delay compensating XUV monochromator [1]. Probing the autoionizing resonance with an IR pulse upon the XUV excitation we observe, that angular distributions of the emitted electron depend on time, which indicates the presence of two coupled states forming the resonance. One of the states has a lifetime of 14 fs, while the lifetime of the other is too short to be detected. Such combination of short and long-lived states is similar to the effect of interference stabilization known in the field of laser-induced interactions and suggests that useful analogies exist between the latter and the field of multielectron dynamics. [1] Eckstein et. al., J. Phys. Chem. Lett. 6, 419 (2015)

MO 15.2 Thu 11:30 f102

**Photoelectron circular dichroism observed in the above-threshold ionization signal from chiral molecules with femtosecond laser pulses** — CHRISTIAN LUX<sup>1</sup>, ARNE SENFTLEBEN<sup>1</sup>, CRISTIAN SARPE<sup>1</sup>, MATTHIAS WOLLENHAUPT<sup>2</sup>, and THOMAS BAUMERT<sup>1</sup> — <sup>1</sup>Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel — <sup>2</sup>Institut für Physik, Carl von Ossietzky Universität Oldenburg, Carl-von-Ossietzky-Straße 9-11, 26129 Oldenburg

Photoelectron circular dichroism (PECD) is investigated experimentally as a function of the number of absorbed circularly polarized photons. Three structurally different chiral molecules yet showing similar absorption spectra are studied. They are isotropically distributed in the gas phase and ionized with femtosecond laser pulses. We measure and analyze the photoelectron angular distribution of threshold electrons ionized with three photons and compare them to those of above-threshold (ATI) electrons ionized with four photons. Additionally to an increase in high even order Legendre polynomials the coefficients of the high odd order Legendre polynomials rise with increasing photon number. Consequently, the ATI electrons also carry the chirality signature. All investigated chiral molecules reveal an individual set of coefficients for the threshold and ATI signatures despite their similarities in chemical structure. The presented data set can serve as a guideline for theoretical modelling of the interaction of circularly polarized light with chiral molecules in the multiphoton regime.

MO 15.3 Thu 11:45 f102

**VUV-induced dissociation of H<sub>2</sub>O studied by single-shot autocorrelation** — ARNE BAUMANN<sup>1</sup>, DIMITRIOS ROMPOTIS<sup>1</sup>, OLIVER SCHEPP<sup>1</sup>, MAREK WIELAND<sup>1,2,3</sup>, and MARKUS DRESCHER<sup>1,2,3</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — <sup>2</sup>The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg, Germany — <sup>3</sup>Centre for Free-Electron-Laser Science (CFEL), Luruper Chaussee 149, 22761 Hamburg, Germany

The femtosecond dissociation dynamics of the water molecule upon excitation into the  $\dot{A}(^1B_1)$  state have been studied by a single-shot autocorrelation pump-probe experiment in the vacuum ultraviolet spectral range. The scheme is based on wave-front splitting of intense Ti:Sa fifth harmonic pulses at 161.8 nm and a colliding pulse geometry, mapping the temporal delay onto a spatial coordinate. This dramatically decreases acquisition time compared to traditional delay-scanning approaches, increasing the statistical precision of the measurement.

Isotope substitution has been utilized to study the primary and secondary kinetic isotope effects on the reaction dynamics of this prototypical over-the-barrier dissociation reaction. Depending on the degree of hydrogen substitution the observed dynamics take place in  $10 \pm 2$  fs

and less.

MO 15.4 Thu 12:00 f102

**Second order interferometric gas-phase autocorrelation in the VUV** — OLIVER SCHEPP<sup>1</sup>, ARNE BAUMANN<sup>1</sup>, THOMAS GEBERT<sup>1,2,3</sup>, DIMITRIOS ROMPOTIS<sup>1</sup>, MAREK WIELAND<sup>1,2,3</sup>, and MARKUS DRESCHER<sup>1,2,3</sup> — <sup>1</sup>Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — <sup>2</sup>The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg, Germany — <sup>3</sup>Centre for Free-Electron-Laser Science, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

We studied the ultrafast photodissociation dynamics of molecules in an VUV-pump VUV-probe scheme using a Michelson-type all-reflective interferometric autocorrelator realized with two moveable interdigitated reflective gratings. An imaging time-of-flight spectrometer is used for separating ions formed in different diffraction orders in the focal plane. In the setup, 18 fs VUV pulses centered at 161.8 nm are created in a variable-length gas cell driven by a Ti:Sa laser and spectrally selected for driving non-resonant two-photon ionization processes. With the fringe-resolved 2nd order autocorrelation in Kr the pulse duration of the VUV pulses was determined. With well-characterized VUV pulses, photo-reaction dynamics of molecular gas targets like O<sub>2</sub> are studied.

MO 15.5 Thu 12:15 f102

**Optimizing sparse sampling patterns for 2D electronic spectroscopy using an evolutionary algorithm** — SEBASTIAN RÖDING<sup>1</sup>, NIKITA KLIMOVICH<sup>1,2</sup>, and TOBIAS BRIKNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Department of Physics, The University of Texas at Austin, Austin, Texas 78712, USA

Recent implementations of coherent two-dimensional (2D) electronic spectroscopy have shown that this technique is not limited to samples in solution. By detecting emitted photoelectrons from a surface [1] or as a photocurrent in a semiconductor nanostructure [2] it became possible to acquire 2D spectra of various types of samples. However, these time-domain experiments suffer from the vast amount of acquisition steps necessary.

We use the paradigm of compressed sensing [3] to reduce the density of sampling points. We employ an evolutionary algorithm to find the best sampling matrix for a data set at a given population time and show how this matrix can be used to measure the same sample at other population times. Furthermore, we discuss the possibility to represent the data on a periodic von Neumann lattice [4] which will be a transform domain with increased sparsity and should further improve signal reconstruction.

[1]Aeschlimann et al., Science 333, 6050 (2011)

[2]Nardin et al., Opt. Express 21, 28617 (2013)

[3]Donoho, IEEE Trans. Inf. Theory 52 (4), 1289 (2006)

[4]Dimler et al., New J. Phys. 11, 105052 (2009)

MO 15.6 Thu 12:30 f102

**Femtosecond oxygen K-edge absorption spectroscopy of thymine** — T. J. A. WOLF<sup>1</sup>, R. HEILEMANN MYHRE<sup>1,2</sup>, H. KOCH<sup>1,2</sup>, A. BATTISTONI<sup>1</sup>, N. BERRAH<sup>3</sup>, P. H. BUCKSBAUM<sup>1</sup>, R. COFFEE<sup>4</sup>, S. CORIANI<sup>5</sup>, G. COSLOVIC<sup>4</sup>, J. CRYAN<sup>1</sup>, R. FEIFEL<sup>6</sup>, K. GAFFNEY<sup>1</sup>, J. GRILJ<sup>7</sup>, T. MARTINEZ<sup>1,8</sup>, S. MIYABE<sup>1</sup>, S. MÖLLER<sup>4</sup>, M. MUCKE<sup>9</sup>, A. NATAN<sup>1</sup>, R. OBAID<sup>3</sup>, T. OSIPOV<sup>4</sup>, O. PLEKAN<sup>10</sup>, A. SAGE<sup>3</sup>, R. SQUIBB<sup>6</sup>, S. WANG<sup>1</sup>, and M. GÜHR<sup>1,11</sup> — <sup>1</sup>PULSE, SLAC National Accelerator Laboratory and Stanford University, USA — <sup>2</sup>Chemistry Dept., NTNU, Trondheim, Norway — <sup>3</sup>Physics Dept., University of Connecticut, Storrs USA — <sup>4</sup>LCLS, SLAC National Accelerator Laboratory, USA — <sup>5</sup>Chemistry Dept., Università di Trieste, Italy — <sup>6</sup>Physics Dept., Gotheborg University, Sweden — <sup>7</sup>LSU, EPFL, Lausanne, Switzerland — <sup>8</sup>Chemistry Dept., Stanford University, USA — <sup>9</sup>Physics Dept., Uppsala University, Sweden — <sup>10</sup>Sincrotrone Elettra, Trieste, Italy — <sup>11</sup>Physics and Astronomy, Universität Potsdam, Germany

We show first results of ultrafast soft x-ray absorption spectroscopy in the gas phase. After ultraviolet excitation to the  $\pi\pi^*$  state, the nucleobase thymine undergoes internal conversion to the  $n\pi^*$  and electronic

ground state. We probe this nonadiabatic process using resonant absorption at the oxygen K-edge. We identify a UV induced bleach of the initially unoccupied  $\pi^*$  states around 531 eV in the absorption spectrum. In addition, we observe an entirely UV generated absorption feature about 4.5 eV lower than the  $\pi^*$  resonances, which we assign to a molecular nonadiabatic relaxation channel.

MO 15.7 Thu 12:45 f102

**Temporal resolution in noisy-pulse transient absorption spectroscopy** — ●KRISTINA MEYER<sup>1</sup>, NIKLAS MÜLLER<sup>1</sup>, ZUOYE LIU<sup>1,2</sup>, and THOMAS PFEIFER<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — <sup>2</sup>School of Nuclear Science and Technology, Lanzhou University, 730000 Lanzhou, China  
Pump-probe experiments with deuterium molecules using Free-Electron-Laser (FEL) pulses revealed molecular dynamics on time scales shorter than the average pulse duration [1]. This enhanced temporal resolution was explained by the partially coherent nature of the FEL pulses [2] and a temporal correlation between the pump and probe pulses. The average spectrum of the FEL pulses provides a coherence time much shorter than the average pulse duration, which is the ultimate limit of temporal resolution instead of the average duration of the noisy, fluctuating pulse shape. Here, we demonstrate the generalization of this noisy-pulse concept to time-resolved spectroscopy in complex systems in the liquid phase. Using a pulse shaper we generated partially coherent laser pulses in the visible to near-infrared range and performed transient-absorption measurements in a solution of the dye IR144 in methanol. Features occurring on time scales ( $\sim 60$

fs) shorter than the average pulse duration (300 fs) could be identified in the measured absorption spectra. Thus, we demonstrate the universality of the concept of achieving a temporal resolution beyond the average pulse duration with statistically fluctuating pulses. [1] Y. Jiang et al., PRA 81, 051402(R) (2010), [2] K. Meyer et al., PRL 108, 098302 (2012)

MO 15.8 Thu 13:00 f102

**Diffraction imaging of a molecular rotational wavepacket with femtosecond MeV electron pulses** — J. YANG<sup>1</sup>, ●M. GÜHR<sup>2,3</sup>, TH. VECCHIONE<sup>2</sup>, M. S. ROBINSON<sup>1</sup>, R. LI<sup>2</sup>, N. HARTMANN<sup>2</sup>, X. SHEN<sup>2</sup>, R. COFFEE<sup>2</sup>, J. CORBETT<sup>2</sup>, A. FRY<sup>2</sup>, K. GAFFNEY<sup>2</sup>, T. GORKHOVER<sup>2</sup>, C. HAST<sup>2</sup>, K. JOBE<sup>2</sup>, I. MAKASYUK<sup>2</sup>, A. REID<sup>2</sup>, J.S. ROBINSON<sup>2</sup>, S. VETTER<sup>2</sup>, F. WANG<sup>2</sup>, S. WEATHERSBY<sup>2</sup>, C. YONEDA<sup>2</sup>, M. CENTURION<sup>1</sup>, and X. WANG<sup>2</sup> — <sup>1</sup>Physics Dept., University of Nebraska, Lincoln, USA — <sup>2</sup>SLAC National Accelerator Laboratory, Menlo Park, USA — <sup>3</sup>Physics and Astronomy, Universität Potsdam, Germany

We captured the rotational wavepacket dynamics of nonadiabatically laser-aligned nitrogen molecules with a combination of 100 fs root-mean-squared (RMS) temporal resolution and sub-Angstrom spatial resolution that makes it possible to resolve the position of the nuclei within the molecule. In addition, the diffraction patterns reveal the angular distribution of the molecules, which changes from prolate (aligned) to oblate (anti-aligned) in 300 fs. Our results demonstrate a significant and important step towards making atomically resolved movies of molecular reactions.