

## MO 1: Quantum Control and Femtosecond Spectroscopy 1

Time: Monday 11:00–13:00

Location: f102

MO 1.1 Mon 11:00 f102

**Controlling the ultrafast relaxation dynamics of uracil: A theoretical study** — ●DANIEL KEEFER<sup>1</sup>, SEBASTIAN THALLMAIR<sup>1</sup>, SPIRIDOULA MATSIKA<sup>2</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department Chemie, LMU München — <sup>2</sup>Department of Chemistry, Temple University, Philadelphia, USA

The RNA nucleobase Uracil exhibits ultrafast relaxation dynamics after optical excitation to the second electronically excited state S<sub>2</sub> (first bright state) [1]. With the constantly increasing capabilities of experimental pulse shaping techniques at hand, it is an obvious question how the dynamics of such a biologically relevant molecule can be influenced. We will give theoretical insights on this issue by designing laser pulses with the help of quantum optimal control theory (OCT).

The 2D potential energy surface for the S<sub>2</sub> state of Uracil exhibits a double well structure and contains a conical intersection (CoIn) seam. After excitation to the S<sub>2</sub> state, the nuclear wave packet evolves via a local minimum to the CoIn seam, and subsequently relaxes to the S<sub>1</sub> state. This relaxation process happens on the femtosecond timescale. We optimized laser pulses to influence the ultrafast dynamics in two extreme ways: One goal was to directly steer the wave packet to the conical intersection seam, and thereby to shorten the time for relaxation to the ground state. Another optimization aim was to keep the wave packet in the S<sub>2</sub> state as long as possible by trapping it in the local minimum and potentially prevent relaxation via the CoIn seam.

[1] S. Matsika et al., *J. Phys. Chem. A* **117** (2013), 12796.

MO 1.2 Mon 11:15 f102

**Rydberg contributions in angular dependent strong field ionization** — ●ROBERT SIEMERING<sup>1</sup>, BETHANY JOCHIM<sup>2</sup>, MOHAMMAD ZOHRABI<sup>2</sup>, ALEKSEY VOZNYUK<sup>4</sup>, JACOB MAHOWALD<sup>4</sup>, DYLAN SCHMITZ<sup>4</sup>, KELSIE BETSCH<sup>2</sup>, BEN BERRY<sup>2</sup>, TRAVIS SEVERT<sup>2</sup>, NORA KLING<sup>2,3</sup>, TIM BURWITZ<sup>4</sup>, KEVIN CARNES<sup>2</sup>, MATTHIAS KLING<sup>2,3</sup>, ITZIK BEN-ITZHAK<sup>2</sup>, ERIC WELLS<sup>4</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität, München, Germany — <sup>2</sup>J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS 66506 USA — <sup>3</sup>Max Planck Institute of Quantum Optics, Garching, Germany — <sup>4</sup>Department of Physics, Augustana University, Sioux Falls, SD 57197 USA

Much of our intuition about strong-field processes is built upon studies of diatomic molecules which have electronic states that are relatively well separated in energy. In polyatomic molecules, however, the electronic states are closer together, leading to more complex dynamics. We investigate experimentally and theoretically the strong-field ionization followed by hydrogen elimination for the hydrocarbon series C<sub>2</sub>D<sub>2</sub>, C<sub>2</sub>D<sub>4</sub>, and C<sub>2</sub>D<sub>6</sub>. Our findings suggest that one has to take into account the shape of the field dressed orbitals rather than the field free orbitals in order to interpret the experimental measurements. The Rydberg character contribution to these field dressed orbitals in strong-field ionization has to be considered to explain the photofragment angular distribution. This improved understanding can facilitate efforts at image-based strong-field coherent control.

MO 1.3 Mon 11:30 f102

**Controlling the dynamics of chemical reactions with tailored laser fields** — ●ROBERT SIEMERING<sup>1</sup>, MATTHIAS KÜBEL<sup>2</sup>, CHRISTIAN BURGER<sup>2</sup>, NORA KLING<sup>2</sup>, HUI LI<sup>2</sup>, BORIS BERGUES<sup>2</sup>, ALI ALNASAR<sup>3</sup>, ITZIK BEN-ITZHAK<sup>4</sup>, MATTHIAS KLING<sup>2</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität, München, Germany — <sup>2</sup>Max Planck Institute of Quantum Optics, Garching, Germany — <sup>3</sup>Physics Department, American University of Sharjah, POB26666, Sharjah, UAE — <sup>4</sup>J.R. Macdonald Laboratory, Physics Department, Kansas-State University, Manhattan, KS66506, USA

The rearrangement of hydrocarbon bonds is a ubiquitous process in chemical reactions related to biology, combustion, and catalysis. Thus, the ability to control the movement of nuclei with tailored light within a hydrocarbon molecule holds promise for far-reaching applications. We demonstrate by experiment and theory the steering of deprotonation from symmetric acetylene molecules and of hydrogen migration in simple hydrocarbons, namely acetylene and allene, using waveform-controlled, few-cycle laser pulses. The rearrangement dynamics are monitored using coincident 3D momentum imaging spectroscopy, and

described with a quantum-dynamical model. Our observations reveal that the underlying control mechanism is due to the manipulation of the phases in a vibrational wavepacket by the intense off-resonant laser field. This mechanism permits control over the directionality of chemical reactions via vibrational excitation on timescales defined by the subcycle evolution of the laser waveform.

MO 1.4 Mon 11:45 f102

**Nuclear spin coherence in the positively charged Nitrogen-Vacancy center in diamond** — ●HELMUT FEDDER<sup>1</sup>, SINA BURK<sup>1</sup>, MATTHIAS PFENDER<sup>1</sup>, NABEEL ASLAM<sup>1</sup>, SEBASTIAN ZAISER<sup>1</sup>, PHILIPP NEUMANN<sup>1</sup>, ANDREJ DENISENKO<sup>1</sup>, PATRICK SIMON<sup>2</sup>, JOSÉ GARRIDO<sup>2</sup>, MARTIN STUTZMANN<sup>2</sup>, MARCUS DOHERTY<sup>3</sup>, NEIL MANSON<sup>3</sup>, AUDRIUS ALKAUSKAS<sup>4</sup>, and JÖRG WRACHTRUP<sup>1</sup> — <sup>1</sup>3. Physikalisches Institut, Uni Stuttgart — <sup>2</sup>Walter Schottky Institut, TU München — <sup>3</sup>Australian National University, Canberra, Australia — <sup>4</sup>Center for Physical Sciences and Technology, Lithuania

Electron and nuclear spins associated with point defects in semiconductors are promising systems for solid state quantum technologies with applications in quantum information processing and quantum sensing. In a typical quantum register architecture, an electron spin is used as an ancilla for readout and control, whereas nuclear spins serve as register qubits [1-2]. Flip-flop processes of the electron spin limit the nuclear spin coherence time. This limitation can be overcome by controlling the defect's ionization state. Here we increase the coherence time of the <sup>14</sup>N nuclear spin associated with the Nitrogen-Vacancy center in diamond by controlling its charge state. We exploit planar double junction diodes fabricated by surface transfer doping with hydrogen [3] to rapidly switch the charge state from NV<sup>-</sup> (S=1) to NV<sup>+</sup> (S=0). We verify the NV<sup>+</sup> state by nuclear magnetic resonance and demonstrate the enhancement of the <sup>14</sup>N coherence time. [1] Saeedi et al., *Science* **342**, 830 (2013). [2] P.C. Maurer et al., *Science* **336**, 1283 (2012). [3] M. Hauf et al., *Nano Lett.* **14**, 2359 (2014)

MO 1.5 Mon 12:00 f102

**Femtosecond dynamics of isolated radicals in the gas phase** — ●ANJA ROEDER<sup>1</sup>, LIONEL POISSON<sup>2</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>University of Wuerzburg, Am Hubland Süd 97074 Wuerzburg, Germany — <sup>2</sup>EA, Laboratoire Francis Perrin-Bât 522 91191 Gif-sur-Yvette, France

Radicals are important intermediates in combustion processes and in the formation of polyaromatic hydrocarbons (PAHs), a precursor to soot. The benzyl radicals were produced from nitrite precursors via pyrolysis and subsequently expanded in a molecular beam. Using femtosecond pump-probe spectroscopy the lifetimes of their excited states were examined via photoelectron spectroscopy and mass spectroscopy. The benzyl radical was excited in the D<sub>5</sub> state using 266 nm and ionized with either a 800 nm or the BBO-doubled 400 nm probe pulse. The dynamics of the D<sub>5</sub>-state was examined using time-resolved mass spectra and time-resolved photoelectron spectra. The results obtained can be understood in framework of the calculations performed by the group of R. Mitric (Wuerzburg), in which the initial populated D<sub>5</sub> state decays quickly via the D<sub>4</sub> to the D<sub>3</sub> state (short time constant), which decays more slowly to the D<sub>1</sub> state (long time constant).

Acknowledgements: Roland Mitric

MO 1.6 Mon 12:15 f102

**Time-resolved Circular Dichroism Spectroscopy of Hemoglobin** — ●HEIKO HILDENBRAND, ANDREAS STEINBACHER, FEDERICO KOCH, MARCO SCHMID, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Circular dichroism (CD) is a common technique to analyze chiral samples. However, the typically utilized long optical path lengths, high concentrations, and long integration times in the steady state are not suitable for ultrafast spectroscopy. Hence, only few chirality-sensitive spectroscopic approaches in the liquid phase are known in the literature [1].

Here, we present broadband time-resolved CD spectroscopy which is based on a setup capable of mirroring an arbitrary polarization state of an ultrashort laser pulse. Hence, by passing a broadband probe pulse through this setup we can switch between opposite handedness on a shot-to-shot basis to detect pump-induced CD changes. To demon-

strate the capabilities of this approach we investigated the early photochemistry of oxygenated hemoglobin and myoglobin by time-resolved circular dichroism and transient absorption spectroscopy in the visible spectral region, since the spectrometer is also capable of acquiring both signals simultaneously.

[1] Meyer-Ilse et al., *Laser Photon. Rev.* 7, 495 (2013)

MO 1.7 Mon 12:30 f102

**Capturing Charge Transfer Dynamics at Dye - Semiconductor Interfaces by Means of Ultrafast XUV Photoelectron Spectroscopy** — •MARIO BORGWARDT<sup>1</sup>, MARTIN WILKE<sup>1</sup>, LEONE SPICCIA<sup>2</sup>, KATHRIN M. LANGE<sup>3</sup>, IGOR YU. KIYAN<sup>1</sup>, and EMAD F. AZIZ<sup>1</sup> — <sup>1</sup>Institute of Methods for Material Development, Helmholtz-Zentrum Berlin, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany — <sup>2</sup>School of Chemistry and ARC Centre of Excellence for Electromaterials Science (ACES), Monash University, Clayton 3800, VIC, Australia — <sup>3</sup>Institute of Solar Fuels, Helmholtz-Zentrum Berlin, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany

We present time-resolved XUV photoelectron spectroscopy as a tool to investigate the ultrafast charge transfer processes at the interface between Ru polypyridyl complexes and various semiconductor nanoparticles. To monitor the electron density distribution among the ground as well as the excited states at the interface XUV light from high-order harmonic generation is used as a probe after exposure with a pump laser pulse in the visible wavelength range. With this approach, we identified for the first time directly the absolute binding energies of the involved charge-transfer states and could provide a comprehensive characterization of the analyzed interfaces. [1] The advantage of studying simultaneously injection kinetics and the electronic structure will

be discussed and an outlook for future applications of this method in view of other promising energy related materials will be presented.

[1] Borgwardt, M. et al. *J. Phys. Chem. C* 2015, 119 (17), 9099-9107.

MO 1.8 Mon 12:45 f102

**Wavelength dependence of Photoelectron Circular Dichroism in Femtosecond Multiphoton Ionization** — •ALEXANDER KASTNER, STEFANIE ZÜLLIGHOVEN, TOM RING, CRISTIAN SARPE, CHRISTIAN LUX, ARNE SENFLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, 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]. We observed highly structured asymmetries in the range of  $\pm 10\%$  on bicyclic Ketones [2, 3]. Due to the multi-photon ionization (MPI), high order Legendre polynomials appear in the measured PADs. In the case of Resonance Enhanced MPI (REMPI) using femtosecond laser pulses, the observed Legendre polynomial distribution is determined through the intermediate resonance and can be influenced by the laser wavelength. In this contribution we show our recent findings on wavelength dependence of the PECD effect of bicyclic Ketones.

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

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

[3] C. Lux et al., *Chem. Phys. Chem*, DOI: 10.1002/cphc.200 (2015)