

## MO 6: Femtosecond Spectroscopy I

Time: Monday 16:30–19:00

Location: V38.03

MO 6.1 Mon 16:30 V38.03

**CRASY: Correlated Rotational Alignment Spectroscopy with 70 MHz resolution** — ●CHRISTIAN SCHRÖTER and THOMAS SCHULTZ — Max-Born-Institut, Berlin

Our aim is the investigation of photochemical reactions in biological chromophores, such as DNA-bases. Biological chromophores can occur in different structural conformations, and the assignment of spectroscopic data to a specific molecular structure is difficult. With CRASY, we are able to measure correlated data to characterize nuclear and electronic structure simultaneously (1). CRASY is a method which combines rotational spectroscopy in the time domain with femtosecond-pump-probe experiments. An IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay, we probe the wave packet by a UV pulse which excites and ionizes the molecule via a resonant electronic state. A Fourier transform of collected electron and ion signals reveals the rotational Raman spectrum for each species in the sample. For the reliable assignment of biomolecular isomers, we require a good rotational resolution. Here we present CRASY measurements with a resolution below 70 MHz, sufficient for the characterization of DNA-base tautomers.

(1) Science 333, 1011 (2011)

MO 6.2 Mon 16:45 V38.03

**Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone observed via Multiphoton Ionization** — ●CHRISTIAN LUX, TOM BOLZE, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSA/T, D-34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) [1] was investigated the last decade on small chiral molecules using vacuum ultraviolet (VUV) synchrotron radiation. The observed asymmetries in PECD arise in forward/backward direction with respect to the light propagation and show an effect several orders larger than in conventionally observed CD. Resonance Enhanced Multi-Photon Ionization (REMPI) in mass spectroscopy of chiral molecules using ultrashort laser pulses [2,3] in the visible and near UV showed also strong asymmetries in the absorption of circularly polarized light.

In this contribution we present that PECD is also accessible using REMPI with UV femtosecond laser pulses [4]. The obtained Photoelectron Angular Distributions in the 2+1 REMPI of Camphor and Fenchone contain highly structured asymmetries up to 20%.

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

[2] C. Logé, A. Bornschlegel, U. Boesl, Anal. Bioanal. Chem. 395, 1631-1639 (2009)

[3] P. Horsch, G. Urbasch, K.-M. Weitzel, Z. Phys. Chem. 225, 587-594 (2011)

[4] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, C. Sarpe, T. Baumert (*in preparation*) (2011)

MO 6.3 Mon 17:00 V38.03

**Magic-angle and anisotropy calculations for arbitrarily polarized pump-probe spectroscopy** — JOHANNES BUBACK, ●SEBASTIAN SCHOTT, ANDREAS STEINBACHER, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We calculate anisotropy effects in pump-probe transient-absorption experiments with arbitrarily polarized pump and probe pulses. The versatility of the approach allows us to simulate various experimental scenarios, e.g. with femtosecond laser pulses generated by a polarization pulse shaper, and to derive magic-angle conditions for which the pump-probe signal is independent of the angle between pump and probe transition dipole moments. Whereas this is well-known for studies with linearly polarized pump and probe pulses, we discuss specifically the case of a polarization-shaped pump pulse for quantum control experiments, as well as the case of a circularly polarized probe pulse for transient circular-dichroism measurements.

MO 6.4 Mon 17:15 V38.03

**Pump-Probe simulations for single trapped molecular ions** — ●MARKUS KOWALEWSKI<sup>1</sup>, STEFFEN KAHRA<sup>2</sup>, GÜNTHER LESCHHORN<sup>2</sup>,

TOBIAS SCHAETZ<sup>2,3</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department Chemie, Ludwigs-Maximilians Universität München — <sup>2</sup>Max-Planck-Institut für Quantenoptik, Garching — <sup>3</sup>Albert-Ludwigs-Universität, Freiburg

Ion traps offer a great possibility to handle cold single molecular ions without environmental interactions. Ultrashort and intense laser pulses are a well established tool for studying and controlling the molecular dynamics. Both methods are combined in a new experiment with MgH<sup>+</sup> ions. It is demonstrated, that a pump-probe experiment under these conditions is possible.

In this talk we present the theoretical model which faces the the problems arising in this novel parameter regime. In contrast to femtosecond experiments in the gas or condensed phase the same molecule is excited by the laser several times. Thus they are subject to internal heating, which has to be treated in the theory and handled in the experiment. Moreover an extended pump-probe pulse scheme is developed which keeps the ions cool.

MO 6.5 Mon 17:30 V38.03

**Simulation of Vibrational Dephasing of I<sub>2</sub> in a Krypton Matrix** — ●MAX BUCHHOLZ<sup>1</sup>, FRANK GROSSMANN<sup>1</sup>, and BURKHARD SCHMIDT<sup>2</sup> — <sup>1</sup>Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden — <sup>2</sup>Institut für Mathematik, Freie Universität Berlin, Arnimallee 6, 14195 Berlin-Dahlem

In four-wave mixing experiments on iodine in a krypton matrix in the Apkarian group [M. Karavitis et al, Phys. Chem. Chem. Phys. 7, 791 (2005)], the decay of coherences between vibrational eigenstates in the electronic ground state of the iodine molecule has been investigated for a range of eigenstates and temperatures. Motivated by these experiments, we study the dynamics of an I<sub>2</sub> molecule in the first micro-solvation shell comprising a Kr<sub>17</sub> double icosahedron using numerical quantum-dynamic models as well as a linearized semiclassical IVR approach [X. Sun and W. H. Miller, J. Chem. Phys. 110, 6635 (1999)]. We are trying to reproduce the experimental decoherence rates by making use of a reduced dimensionality model consisting of krypton ("bath") modes with different coupling to the I<sub>2</sub> vibrational ("system") mode.

This work was supported by the DFG through grant GR 1210/4-2.

MO 6.6 Mon 17:45 V38.03

**Weak field, multiple cycle carrier envelope phase effects in laser excitation** — ●KLAUS RENZIEHAUSEN and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg

Whereas the absolute or carrier envelope phase (CEP) of a laser pulse is usually assumed to be effective for ultrashort and/or ultrastrong pulses only, we demonstrate that these limitations can be removed. For an initial population distribution between different states of a quantum system interacting with an external field, it is possible to influence the population transfer in changing the CEP. Analytical results for a two-level system are presented. In a numerical example, we treat molecular excitation, where vibrational manifolds in two electronic states of the sodium dimer are coupled by the laser field.

MO 6.7 Mon 18:00 V38.03

**Carrier envelope phase controlled dynamics at conical intersections** — ●ROBERT SIEMERING, PHILIPP VON DEN HOFF, and REGINA DE VIVIE-RIEDLE — Department Chemie Ludwig-Maximilians-Universität München, Butenandtstr. 11, Haus E, 81377 München, Germany

We investigate how ultrafast dynamics at conical intersection can be combined with laser control schemes. Therefore we study the effect of the non-adiabatic-coupling for wavepackets approaching the conical intersection from different directions and different momenta in model systems. These two dimensional model systems are set up in the g/h-plane (branching space) of the conical intersection between two potential energy surfaces. We analyse the relationship between transfer efficiency and the initial conditions of the wavepacket. Based on these results we develop a control scheme that relies on the carrier envelope phase of the control laser pulse. The control scheme includes

the creation of an electronic superposition state before the wavepacket reaches the conical intersection. The control landscape is enhanced by applying optimal control strategies. To optimize carrier envelope phase control within optimal control theory we used its phase sensitive variant.

MO 6.8 Mon 18:15 V38.03

#### Efficient sub-cycle control of electron dynamics in molecules

— ●HENDRIKE BRAUN<sup>1</sup>, TIM BAYER<sup>1</sup>, CRISTIAN SARPE<sup>1</sup>, ROBERT SIEMERING<sup>2</sup>, PHILIPP VON DEN HOFF<sup>2</sup>, REGINA DE VIVIE-RIEDLE<sup>2</sup>, MATTHIAS WOLLENHAUPT<sup>1</sup>, and THOMAS BAUMERT<sup>1</sup> — <sup>1</sup>University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany — <sup>2</sup>Ludwig-Maximilians-Universität München, Departement Chemie, D-81377 München, Germany

Shaped femtosecond laser pulses are a well established tool to control the dynamics of the nuclei within a molecule after electronic excitation. Here we demonstrate that the electron dynamics of a molecule can also be efficiently manipulated by controlling the temporal phase of a femtosecond laser pulse. Specifically, we show how temporal phase changes on the time scale of the electron motion, i.e. with sub-cycle precision, are used to manipulate the electron dynamics of molecules and eventually switch between different potential energy surfaces of the molecule. The underlying control mechanism is termed SPODS (Selective Population of Dressed States) and has already been demonstrated on atoms [1,2,3]. It relies on the resonant excitation of an *electronic* coherence and subcycle control of the phase relation of the corresponding electric dipole and the strong light field. Extension to molecular systems shows the prospect of various applications of SPODS in femtochemistry.

- [1] M. Wollenhaupt *et al.*, Phys. Rev. A **68**, 0154011 (2003)
- [2] M. Wollenhaupt *et al.*, Phys. Rev. A **73**, 063409-1 (2006)
- [3] T. Bayer *et al.*, Phys. Rev. Lett. **102**, 023004 (2009)
- [4] M. Wollenhaupt *et al.*, JPPA **180**, 248 (2006)

MO 6.9 Mon 18:30 V38.03

#### Selective population of dressed states: A robust path-

way to populate selectively higher lying electronic states in molecules? — ●PHILIPP VON DEN HOFF<sup>1</sup>, HENDRIKE BRAUN<sup>2</sup>, TIM BAYER<sup>2</sup>, MATTHIAS WOLLENHAUPT<sup>2</sup>, THOMAS BAUMERT<sup>2</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität München, Departement Chemie, Germany — <sup>2</sup>University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

Selective population of dressed states (SPODS) has been proposed as an alternative control pathway in molecular reaction dynamics [1]. Recently, this scenario was successfully implemented in experiments using the molecule K<sub>2</sub>. Based on these results, we investigate if and under which conditions this strong field scheme is included in the search space of optimal control theory (OCT). Thereby we classify SPODS within the global search space of OCT and discuss the question of robustness. Like in the experiments we use the example of the potassium dimer. Within the SPODS-mechanism different target states can be reached via dressed states by subcycle control of the phase relation of the corresponding electric dipole and the strong light field. Especially, we investigate whether the optimization algorithm is able to find the route involving the dressed states although the target state lies out of resonance in the bare state picture.

- [1] M. Wollenhaupt *et al.*, Phys. Rev. A **68**, 0154011 (2003)

MO 6.10 Mon 18:45 V38.03

**Attosecond dynamics of CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>** — ●CHRISTIAN NEIDEL, JESSE KLEI, CHUNG-HSIN YANG, and MARC VRACKING — Max-Born-Institut

We report the first attosecond time-resolved measurements for the molecules CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. Angular resolved photoelectron and photoion yields were characterized with a velocity map imaging spectrometer (VMIS). Different fragments like O<sup>+</sup> and H<sup>+</sup> were produced by dissociative ionization. The signal yields show clear oscillations with respect to the time delay between an attosecond pulse train (APT) and a femtosecond IR pulse. The ionization process is modulated by coupling of molecular states by the IR field. The results demonstrate the feasibility of attosecond experiments for larger molecules.