MO 3: Femtosecond Spectroscopy 1

Time: Monday 14:30–16:30 Location: PH/HS1

Invited Talk MO 3.1 Mon 14:30 PH/HS1

Vibrational coherence in excited electronic states studied with multidimensional time-resolved spectroscopy — Tiago Buckup and •Marcus Motzkus — Physikalisch-Chemisches Institut, Ruprecht-Karls Universität, D-69120 Heidelberg, Germany

Multidimensional femtosecond time-resolved vibrational coherence spectroscopy allows one to studying the evolution of vibrational coherence in electronic excited states. Methods like pump-DFWM and pump-IVS combines an initial ultrashort laser pulse with a nonlinear probing sequence to re-induce vibrational coherence exclusively in the excited states. By carefully exploiting specific electronic resonances, vibrational coherence from 0 cm-1 over 2000 cm-1 can be detected and its evolution can be mapped. This talk focuses on the observation and mapping of high-frequency vibrational coherence for all-trans biological polyenes like lycopene, retinal and retinal Schiff base. We discuss the role of molecular symmetry in the vibrational coherence activity in the S1 electronic state and the interplay of coupling between electronic states and vibrational coherence.

[1] T. Buckup and M. Motzkus, Annual. Rev. Phys. Chem. 65 (2014) 39.

MO 3.2 Mon 15:00 PH/HS1

Unraveling photochemical reaction pathways of diphenylcarbene in solvent mixtures — •Johannes Knorr[1], Sebastian Schott[2], Paolo Costa[3], Wolfram Sander[3], and Patrick Nuernberger[1] — [1]Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — [2]Institut für Physikalische und Theoretische Chemie, Am Hubland, Universität Würzburg, 97074 Würzburg — [3]Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

The primary reaction pathways of singlet diphenylcarbene (DPC) in the presence of a solvent can be summarized as an interplay of an intersystem crossing to the triplet state (e.g., in neat acetonitrile) and the formation of an ether product (in alcohols) which can either be formed by reaction with an alcohol in a concerted or stepwise manner or via a short-lived cation resulting from an ultrafast intermolecular proton-transfer reaction [1]. Recent studies on DPC embedded in argon matrices at low temperatures revealed dramatic changes in the reactivity when the carbene environment was modified by small amounts of methanol dopant molecules [2]. Connecting these findings with experiments in the liquid phase at room temperature, we employ femtosecond transient-absorption spectroscopy in the visible and ultraviolet regime to unravel the reactivity of DPC in solvent mixtures. Our studies corroborate that the dynamics are far from a linear combination of those observed in neat solvents, with the efficiency of different reaction channels varying significantly in dependence on the solvent mixing ratio.

[1] J. Peon et al., J. Am. Chem. Soc. 2002, 124, 6428-6438

[2] P. Costa and W. Sander, Angew. Chem. 2014, 53, 5122-5125

MO 3.3 Mon 15:15 PH/HS1

Ultrafast Dynamics of the Low-Temperature Phase of MEH-PPV — •Cristina Consani[1], Federico Koch[1], Fabian Panzer[2], Thomas Unger[2], Anna Köhler[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Lehrstuhl Experimentalphysik II, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth

Understanding the effect of structure and aggregation on exciton transport in polymers is relevant for the design of functional artificial systems for applications in organic photovoltaics.

Here we investigate the process of energy transfer in the low-temperature phase of MEH-PPV, a planarized aggregated phase characterized by an increased conjugation length as compared to the coiled room-temperature phase. By combining transient absorption and coherent two-dimensional spectroscopy we identify the characteristic time scales of energy transfer within the aggregate. Additionally, the possibility to retrieve information on the exciton diffusion from the power dependence of the investigated signal will be discussed.

MO 3.4 Mon 15:30 PH/HS1

Photoelectron Circular Dichroism from Multiphoton Ionization with Femtosecond Laser Pulses — Christian Lux[1], •Alexander Kastner[1], Stefanie Züllighoven[1], Tom Ring[1], Cristian Sarpe[1], Arne Senftleben[1], Matthias Wollenhaupt[2], and Thomas Baumert[1] — [1]Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany — [2]Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26129 Oldenburg, Germany

The asymmetry of photoelectron angular distributions 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]. In our recent publication [2] we demonstrated that PECD is accessible via a Resonance Enhanced Multi-Photon Ionization (REMPI) using femtosecond laser pulses. We observed highly structured asymmetries in the range of ± 10%. Attributed to the MPI high order odd Legendre polynomials appear in the measured PECD. In this talk we show our recent findings in above-threshold ionization and enantiomeric purity studies on bicyclic Ketones. A first test on molecular modification on Phenylethanol is demonstrated. The strength of PECD can be determined by quantitative measures [3].

[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., ChemPhysChem, DOI:10.1002/cphc.201402643

MO 3.5 Mon 15:45 PH/HS1

Chiral Distinction via Femtosecond Mass Spectrometry with a Twin Peak Ion Source — Christian Lux[1], •Tom Ring[1], Stefanie Züllighoven[1], Alexander Kastner[1], Cristian Sarpe[1], Arne Senftleben[1], Matthias Wollenhaupt[2], and Thomas Baumert[1] — [1]Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel — [2]Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26129 Oldenburg

Circular dichroism (CD) in laser mass spectrometry gives access to the distinction of chiral molecules in the gas phase [1,2]. A twin mass peak setup allows circumventing shot-to-shot fluctuations in laser pulse intensity, gas density or ion detection. Two foci with a small spatial displacement result in time-separated mass spectra. A change in helicity from focus to focus implements a self-referencing system. Using nanosecond laser pulses a back reflecting setup [3] provides the desired characteristics. Due to optical dispersion, this does not work with ultra-short laser pulses. Hence, we introduced an in-line setup applicable for femtosecond laser pulses. In this contribution, we show the advantages of the new optical setup and present our first results of mass-selective chiral analysis via time of flight mass spectrometry.

[1] Titze, Zollitsch, Heiz, Boesl: *ChemPhysChem* **2014**, *15*, 2762-2767

[2] Horsch, Urbasch, Weitzel: *Chirality* **2012**, *24*, 684-690

[3] Logé, Boesl: *ChemPhysChem* **2011**, *12*, 1940-1947

MO 3.6 Mon 16:00 PH/HS1

The photoinduced ring closure of an o-acylbenzaldehyde - Intricate kinetics deciphered by femtosecond spectroscopy and quantum chemistry — •Sascha Fröbel, Laura Buschhaus, Torben Villnow, Oliver Weingart, and Peter Gilch — Heinrich-Heine-Universität Düsseldorf, Germany

The photoinduced ring closure of o-acylbenzaldehydes has been under investigation for decades. Nevertheless, the course of the reaction is not yet completely understood. This can be attributed to the fact that it contains multiple ultrafast processes, which heretofore could not be resolved.

We combined femtosecond absorption techniques and stimulated Raman spectroscopy (FSRS) with quantum chemical computations to study the photoreaction of o-acetylbenzaldehyde in acetonitrile [1]. It turned out that the photochemistry and -physics of this compound are rather complex, involving at least five kinetic processes within the first two nanoseconds after excitation. By FSRS, one of these processes was identified as an intramolecular hydrogen transfer yielding a ketene intermediate. Afterwards the photoproduct, 3-methylphthalide, is formed via an additional intermediate with a lifetime of more than 100 microseconds.

[1]S. Fröbel et al., Phys.Chem.Chem.Phys. 2015, 17, 376-386.

MO 3.7 Mon 16:15 PH/HS1

Ultrafast photophysics of a DNA intercalated psoralen —

Sascha Fröbel, •Anna Reiffers, and Peter Gilch — Heinrich-Heine-Universität Düsseldorf, Germany

After we have studied the formation of photolesions within DNA in the past (see e.g. [1]), we have now extended our studies to photolesions induced by intercalated compounds.

A model system for such compounds are psoralens. Psoralens are heterocyclic natural compounds with various applications in the research lab. Apart from this they are primarily known for their use in the treatment of common skin disorders like psoriasis and vitiligo (PUVA (psoralen + UV-A light) therapy). Their function in PUVA therapy is correlated to their intercalation into DNA. Upon photo excitation, intercalated psoralens form [2+2] cycloadducts with thymines and thus damage the host cells. However, the ultrafast photochemical and -physical processes after excitation are still fully unknown.

We have studied the interactions of an intercalated psoralen (4'-aminomethyl-4,5',8-trimethylpsoralen, AMT) with DNA by means of femtosecond transient absorption for the first time. In DNA the fluorescence lifetime is reduced to 4 ps as compared to 1.4 ns for free AMT. This prohibits the population of triplet states. Instead, an unanticipated intermediate with a lifetime of 30 ps is formed, which is assigned to an electron transfer product. Hereby, the DNA acts as an electron donor.

[1]W.J. Schreier et al., Science 2007, 315, 625./G. Ryseck et al., Chem.Phys.Chem. 2011, 12, 1880.