

MO 22: Femtosecond Spectroscopy 3

Time: Friday 11:00–13:00

Location: PH/HS1

MO 22.1 Fri 11:00 PH/HS1

Effects of Conjugation on Molecular Dynamics — ●FEDERICO KOCH¹, ANDRÉ ZITZLER-KUNKEL², CRISTINA CONSANI¹, FRANK WÜRTHNER², and TOBIAS BRIKNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Interactions of chromophores and formation of excitons play a fundamental role in understanding the dynamics of molecules ranging from small molecular systems up to complex systems such as polymers and aggregates. To better understand these interactions a series of merocyanine dyes directly linked via a bridge was synthesized. This molecular series allows the comparison between interactions through space and interaction mediated by the bridge.

The differences in the absorption maxima and band splitting can in principle be explained by a vibrational progression or a weak excitonic coupling. To investigate this we use transient absorption and compare the relaxation dynamics after excitation. Furthermore, we aim to directly visualize chromophore interaction by using polarization-dependent measurements and coherent 2D spectroscopy.

MO 22.2 Fri 11:15 PH/HS1

Phase-modulated fs pump-probe spectroscopy of RbHe exciplexes — ●LUKAS BRUDER, MARCEL BINZ, AARON LAFORGE, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Due to the low target densities in molecular and doped He droplet beam experiments, coherent fs spectroscopy in such setups has remained a challenging task. In this context we are investigating a phase-modulation fs pump-probe technique established by Marcus et al. [1]. The combination of continuous acousto-optical phase modulation with lock-in detection greatly improves the signal-to-noise ratio in this scheme. We have applied this method to our He droplet beam apparatus and acquired mass-resolved photo ionization spectra of RbHe exciplexes. This data reveals much higher resolution than was previously achieved with conventional pump-probe setups. Furthermore, one gains new insight into the energy structure of the exciplex.

[1] P. F. Tekavec, T. R. Dyke, and A. H. Marcus, *J. Chem. Phys.* 125, 194303 (2006).

MO 22.3 Fri 11:30 PH/HS1

Comparative quantum dynamical studies of two diphenylmethyl halide species in a quasi-diabatic picture states including three-state conical intersections — ●MATTHIAS K. ROOS, SEBASTIAN THALLMAIR, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Carbocations and -radicals are key intermediates of many reactions both in organic synthesis and biochemistry. Such reactive species can be generated by UV laser irradiation of diphenylmethyl halides. This so triggered sub-picosecond ultrafast dissociation occurs via a local π - π^* excitation and finally the carbon-halide σ -bond cleavage is either homolytic or heterolytic. The halide, i.e. chlorine or bromine, acts as leaving group. We use both quantum chemical and quantum dynamical methods to model the bond cleavage and evaluate the branching ratio between the two product pathways. Based on a reduced coordinate space that explicitly includes geometry relaxation for the carbon skeleton the kinetic Hamiltonian is expressed via the Wilson G-Matrix approach. Potential energy surfaces are calculated on the ONIOM(CASSCF(12,10)/B3LPYP) level of theory showing consecutive conical intersections near the Franck-Condon region. Especially three-state conical intersections play the key role for the product splitting. Using *ab initio* properties the adiabatic potentials are transformed to a quasi-diabatic picture, therefore the off-diagonal potential terms are accounting for the non-adiabatic behaviour. The dynamics for both leaving groups is discussed and compared with experimental results.

MO 22.4 Fri 11:45 PH/HS1

Towards multi-dimensional Raman spectroscopy of excited electronic states in the time domain — ●TORSTEN WENDE, CHRISTOPH SCHNEDERMANN, MATZ LIEBEL, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road,

Oxford OX1 3QZ

Many biological and chemical processes rely on an efficient transfer of photon energy into specific atomic motion. Following the nuclear motion directly after photoexcitation provides valuable structural information to elucidate the mechanism that governs the energy flow throughout a molecule. We have developed a time-domain approach for measuring time-resolved excited-state Raman spectra by means of population-controlled impulsive vibrational spectroscopy. Using an ultrashort actinic (<15 fs) and impulsive (<10 fs) pump pulse in combination with a narrowband dump control pulse allows us to experimentally isolate excited-state vibrational coherence and follow its temporal evolution. Here, we study the fast internal conversion (<100 fs) from the S2 into the S1 electronic state in diphenyl-octatetraene. The time-resolved Raman spectra reveal that vibrational coherence is efficiently transferred from S2 into S1. We observe large amplitudes in the 850, 1300 and 1550 cm⁻¹ modes which decay according to the S2 lifetime, while the remaining modes decay primarily with the lifetime of S1. Extraction of a 2D correlation map exhibits signatures of vibrational coupling indicated by multiple cross-peaks between low-frequency modes and selected high-frequency modes.

MO 22.5 Fri 12:00 PH/HS1

Surface-Enhanced, 2D Attenuated Total Reflectance Infrared Spectroscopy At Solid-Liquid Interfaces — ●JAN PHILIP KRAACK, DAVIDE LOTTI, and PETER HAMM — Department of Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057

Femtosecond dynamics of molecules at solid-liquid and solid-gas interfaces have recently gained considerable attention in nonlinear spectroscopy. We present recent advances towards establishing a new experimental method which is capable of resolving coherent, ultrafast two-dimensional (2D) infrared (IR) spectra of molecules adsorbed on metallic thin films.(1) The method is based on measuring Attenuated Total Reflectance (ATR) signals at solid-liquid interfaces using metals for immobilization of the samples. We present details of the femtosecond 2D ATR IR technique together with benchmarking results from small molecules as well as organic monolayers.(2) The nonlinear signals are investigated in terms of surface-enhancement effects(3) and environmental interactions. It is demonstrated that 2D ATR IR spectroscopy allows a surface-sensitive characterization of vibrational lifetimes, dephasing, spectral diffusion and sample inhomogeneity on the femtosecond timescale.

(1) Kraack, J. P.; Lotti, D.; Hamm, P., *JPC Lett.* 2014, 18, 2325.

(2) Kraack, J. P.; Lotti, D.; Hamm, P., in preparation.

(3) Donaldson, P. M.; Hamm, P., *Angew. Chemie* 2013, 125, 662.

MO 22.6 Fri 12:15 PH/HS1

Ultrafast Dissociation Dynamics of Superexcited Nitrogen — ●JOHAN HUMMERT¹, MARTIN ECKSTEIN¹, DANIEL STRASSER², MARC J. J. VRAKKING¹, and OLEG KORNILOV¹ — ¹Max Born Institut, Berlin, Germany — ²Institute of Chemistry, The Hebrew University of Jerusalem, Israel

Understanding relaxation pathways of neutral superexcited states in elementary molecules is important to model the chemistry of environments exposed to XUV and other ionizing radiation. Such species occur in terrestrial and extraterrestrial atmospheres and in man-made environments. Additionally the coupling of electronic and nuclear degrees of freedom in superexcited states is particularly interesting since the Born-Oppenheimer approximation is often strongly violated.

In this experimental work we investigate dissociation dynamics of superexcited states of molecular nitrogen excited by pulsed XUV light. We employ a high harmonic generation source in combination with a time-compensating XUV monochromator to select the 15th harmonic of a 790 nm IR laser pulse at 23.6 eV, which is just below the threshold for dissociative ionization of N₂ (24.25 eV). A second laser pulse at the wavelength of 790 nm probes the highly excited molecules or fragments after a time-delay ionizing them to produce the detected N⁺ ions.

The recorded transient signals demonstrate both a very quickly decaying component (about 40 fs) as well as a long-lived contribution. Preliminary assignments suggest competition between predissociation from Rydberg-type states converging to the ionic C²Σ_u⁺ state and autoionization leading to bound ions.

MO 22.7 Fri 12:30 PH/HS1

Reaction-sensitive tracking of ultrafast chemical reaction dynamics with pump-dump spectroscopy — ●ALEX S. DUARTE, GIOVANNI BASSOLINO, CHRISTOPH SCHNEIDERMAN, JONGMIN LIM, TORSTEN WENDE, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

The retinal protonated Schiff base (RPSB) chromophore has become a paradigmatic photochemical system due to its widespread involvement in biological photoreceptors. One of the most puzzling and most studied aspects of RPSB photochemistry is the dramatic increase in reaction speed and yield in the protein over the solution environment, which has been attributed to a specific interaction of the chromophore with an evolution-optimised protein pocket.

Here, we combine excitation of RPSB in solution with a resonant 20 fs optical pulse followed by a 10 fs dump pulse that only serves to control the excited state population. By monitoring the photoproduct formation through changes in the transient absorption spectrum of RPSB at long time delays (60 ps) as a function of pump-dump-delay we reveal the earliest excited state relaxation dynamics for both 11-cis and all-trans RPSB in solution. Remarkably, the experiment reveals an ultrafast (<100 fs) photoisomerization channel for 11-cis RPSB in contrast to all-trans RPSB, closely resembling the dynamic behaviour of 11-cis RPSB in rhodopsin during the first step of vision.

MO 22.8 Fri 12:45 PH/HS1

Real-time tracking of structural rearrangements in wt-GFP after photoexcitation — ●CHRISTOPH SCHNEIDERMAN, TORSTEN WENDE, GIOVANNI BASSOLINO, MATZ LIEBEL, and PHILIPP KUKURA — Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

A vast number of biological and chemical processes rely on the efficient conversion of photon energy into atomic motion. In order to understand the factors determining the energy flow after photoexcitation, it is necessary to track the atomic motion in real-time directly after the absorption of a photon has occurred. Here, we present a time-domain approach capable of resolving the temporal evolution of excited state nuclear degrees of freedom with broadband impulsive vibrational spectroscopy. An actinic pump pulse (15 fs) excites the system followed, after a variable time-delay, by an impulsive Raman pulse (10 fs), which generates vibrational coherences in all excited molecules. These coherences are subsequently recorded by a probe pulse for varying actinic-impulsive pump delay. We use this approach to investigate the excited state proton transfer in wild-type green fluorescent protein and reveal signatures of vibrational coupling between FC and excited state nuclear degrees of freedom akin to multi-dimensional infrared spectroscopy. The observed cross-peaks throughout the fingerprint regime reveal the atomic motions occurring during proton-transfer after photoexcitation.