

MO 10: Femtosecond Spectroscopy II

Time: Tuesday 11:00–12:30

Location: F 102

Invited Talk

MO 10.1 Tue 11:00 F 102

Revealing coherent nuclear wavepacket dynamics in biological photoreceptors — MATZ LIEBEL and PHILIPP KUKURA — Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford

Revealing the atomic motions associated with a chemical transformation to understand the basis of chemical reactivity and dynamics has been one of the most sought after experimental capabilities over the past decades. Transferring the original observation of coherent nuclear wavepacket dynamics in simple diatomics to more complex systems, however, has proved exceedingly difficult. A tremendously well studied example is the all-trans to 13-cis photoisomerisation of the retinal chromophore in bacteriorhodopsin. Despite being subjected to virtually every ultrafast spectroscopic technique, its excited state vibrational spectrum and coherent nuclear dynamics remain largely in the dark. We have developed a novel approach, termed population assisted impulsive Raman spectroscopy (PAIRS), to succeed in not only determining the vibrational spectrum of the reactive excited electronic state, but also the coherent evolution of the photon-induced nuclear wavepacket during the isomerisation reaction. Our results reveal the activation of hydrogen out of plane nuclear motion following relaxation out of the initially populated Franck-Condon region, an emerging trademark of highly efficient C=C isomerisation reactions. The simplicity of the technique, together with a complete lack of often encountered interfering background signals is likely to make PAIRS one of the premier tools for studying ultrafast chemical reaction dynamics.

MO 10.2 Tue 11:30 F 102

Coherent high-frequency vibrational dynamics in the excited electronic state of all-trans retinal derivatives — JAN PHILIP KRAACK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Deutschland.

Coherent vibrational dynamics in excited electronic state(s) of photoactive chromophores are of primary importance in the understanding of photobiology. Using pump-DFWM(1-2), we demonstrate for the first time the existence of coherent high-frequency modulations ($> 1200 \text{ cm}^{-1}$) in the excited electronic state of different retinal derivatives. All-trans retinal as well as retinal n-butyl Schiff-bases exhibit a partial frequency downshift of the C=C double bond mode from around 1580 cm^{-1} in the ground state to 1510 cm^{-1} in the excited state. In addition, a new vibrational band at $\sim 1700 \text{ cm}^{-1}$ assigned to the C=N-stretching mode in retinal Schiff-bases in the excited state is detected. The newly reported bands are observed only if the DFWM-spectrum is tuned to specific spectral regions of excited-state absorption. Implications regarding the observation of vibrational coherences in naturally occurring retinal protonated Schiff-bases in rhodopsins are discussed. (1)Kraack et al., PCCP 2012, 14, 13979. (2)Buckup et al., ABB 2009, 483, 219.

MO 10.3 Tue 11:45 F 102

Time-resolved photoelectron spectroscopy of all-trans retinal in polar and non-polar solvents — KATHRIN MARIA LANGE, MARTIN ECKSTEIN, FRANZISKA BUCHNER, JOHAN HUMMERT, KATRIN HERMANN, WOLFGANG FREYER, ANDREA LÜBCKE, and OLEG KORNILOV — Max-Born Institut, Max-Born-Str. 2a, 12489 Berlin, Deutschland

Retinal is a chromophore of light-sensitive proteins such as rhodopsin

and bacteriorhodopsin. As part of the protein it undergoes very efficient cis-trans isomerization upon absorption of a photon and triggers photoactivity of the biological system. Its dynamics, however, are drastically different in solvent environment and the ordering and lifetimes of excited electronic states in the singlet manifold has long been a matter of controversy, complicating the understanding of the photophysical activity of retinal. In this contribution we present the first results on femtosecond photoelectron spectroscopy of all-trans retinal in the solvents ethanol and n-heptane using the novel liquid micro-jet technology in combination with a Vis-UV pump-probe setup. The time-dependent photoelectron spectra give information on binding energies of the excited states and help to assign relaxation time scales. Influence of solvent polarity on state ordering and decay times will be discussed as well as excitation energy dependence.

MO 10.4 Tue 12:00 F 102

Time-Resolved Vibrational Spectroscopy of a Short-lived Dark Electronic State — MARIE S. MAREK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Dark electronic states play an important role in photobiology. Many photophysical and photochemical processes taking place in biological systems after light absorption such as light-harvesting, vision or photodamage are strongly influenced by the presence of dark states. On the other hand, such dark states are extremely challenging for optical spectroscopy, all the more when they have short lifetimes in the subpicosecond timescale. Here, however, we present direct observation of vibrational coherences in such a short-lived intermediate dark state in a prominent representative of the carotenoid family, spheroidene. Using the method of pump-degenerate four-wave-mixing (pump-DFWM), we are able to follow the wavepacket dynamics from the initially excited S_2 state to the S_1 state via an additional excited electronic state. In Spheroidene, the S_2 state is energetically degenerate with the dark $3A_g^-$ state. A mixing of these two states leads to symmetry breaking and allows for an additional excited state absorption, which is forbidden in the pure states. This ESA appears in the pump-DFWM signal at the same delay as a well-known stimulated emission to a hot ground state and interference between the signals leads to a characteristic splitting of the modes in spheroidene's vibrational spectra for early delays.

MO 10.5 Tue 12:15 F 102

High accuracy measurements of the electron transfer in photosynthetic reaction center of Rhodospira rubra — PABLO NAHUEL DOMINGUEZ, MATTHIAS HIMMELSTOSS, and WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, 80538 München

Rhodospira rubra is a purple bacteria with the most simple and well studied reaction center, which is capable to convert energy from the sunlight into chemical energy via electron transfer and charge separation. This process has four intermediate states, and their observation requires high sensitivity at very low excitation energies. Using new developments in subpicosecond pump-probe spectroscopy, we were able to produce transient absorption spectra for a large set of wavelengths at very low excitation which can be analyzed without any smoothing algorithm. The results confirm the existence of an intermediate radical pair state P^+B^- with a decay time of 0.9ps.