

MO 18: Biomolecules

Time: Thursday 11:00–13:00

Location: PH/SR106

Invited Talk

MO 18.1 Thu 11:00 PH/SR106
cis-trans Isomerization, Ion-Pumps and pH-Sensor: From Molecular Interactions to Biological Function — ●ROLF DILLER¹, PATRICK SINGER¹, MIRIAM COLINDRES¹, PHILIPP ALT¹, EKKEHARD NEUHAUS², and TILMAN LAMPARTER³ — ¹TU Kaiserslautern, Germany — ²TU Kaiserslautern, Germany — ³KIT, Karlsruhe, Germany

Light sensing and photosynthesis are only the most prominent examples for quite many extremely important phenomena in biology that rely on photochemical reactions. In spite of their realization by a relatively small number of chromophores the great functional diversity is facilitated by fine tuned reaction control via balanced chromophore protein interaction. Besides their versatility in biology these systems can be used and adapted for artificial applications in medicine and biological research. This requires the detailed understanding of molecular processes on time scales from femtoseconds to seconds.

Here we focus on photoinduced cis-trans isomerization as fundamental reaction in retinal binding proteins (ion pumps, light sensing) and in bilin binding phytochromes (light sensing). Femtosecond time resolved UV/Vis and infrared vibrational spectroscopy is used to explore electronic and structural dynamics of the cofactor-protein moiety. We report on the ultrafast interaction of the isomerizing retinal chromophore with a water cluster in Bacteriorhodospin and on the biliverdin binding phytochrome Agp2 from *A. tumefaciens* that has been suggested to serve as light-based pH-sensor and exhibits unusual properties involving isomerization of the deprotonated chromophore.

MO 18.2 Thu 11:30 PH/SR106
Structure Determination of *trans*-Cinnamaldehyde using Broadband Microwave Spectroscopy — ●SABRINA ZINN^{1,2,3}, THOMAS BETZ^{1,2,3}, and MELANIE SCHNELL^{1,2,3} — ¹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg/Germany — ²Center for Free-Electron Laser Science, Hamburg/Germany — ³The Hamburg Centre for Ultrafast Imaging, Hamburg/Germany

The high-resolution rotational spectrum of gas-phase *trans*-cinnamaldehyde ((2E)-3-phenylprop-2-enal) has been obtained with chirped-pulse microwave spectroscopy in the frequency range of 2 - 8.5 GHz. The odorant molecule is the essential component in cinnamon oil and causes the characteristic smell. Studying the structure of odorant molecules to learn more about the structure-odor relationship can give insights into molecular recognition by olfactory receptors.

We were able to assign the rotational spectra of *trans*-cinnamaldehyde as well as all single substituted ¹³C-species of the molecule. The change in mass, caused by carbon atom substitution in natural abundance, leads to a change of the molecular moments of inertia and thus of the rotational constants. From these additionally obtained parameters, the molecular structure can be determined by using for example Kraitchman's equations. The obtained structure can be used for a comparison to the structures of other odorant molecules.

MO 18.3 Thu 11:45 PH/SR106
IRMPD spectra of metal-lumiflavin ionic complexes — ●ALAN GÜNTHER¹, PABLO NIETO¹, GIEL BERDEN², JOS OOMENS², JUDITH LANGER¹, and OTTO DOPFER¹ — ¹Institut für Optik und Atomare Physik, TU Berlin, Berlin, Germany — ²Radboud University Nijmegen, Institute for Molecules and Materials FELIX Facility, Nijmegen, The Netherlands

Flavins are a fundamental class of biomolecules with lumiflavin (LF) as its smallest member. They are involved in many important biological processes. For example, as a component of flavo-proteins, they participate in the repair of DNA [1]. To understand these phenomena at the molecular level, spectroscopic studies of the geometric and electronic structure of isolated flavins and their complexes are required. We report IRMPD spectra of mass-selected Me⁺-LF (Me = Li, Na, K, Cs, Cu, Ag) ionic complexes in the fingerprint range (800-1900 cm⁻¹) accompanied by DFT calculations. In solution, metal ions preferentially bind to N5 and O4 of the flavin [2]. In contrast, additional O2 binding sites are identified for all alkali metal ions in our experiments, whereas for Cs⁺ only the O2 position is observed. For Ag⁺ and Cu⁺ only O4 and N5 chelates are identified, although the presence of the O2 isomer cannot be excluded. These metals also bind with different angles compared to alkali metals due to covalent contributions caused by their

electronic configuration. The limited spectral resolution of these experiments will be overcome with our new apparatus equipped with a cryogenic 22-pole ion trap. [1] M. Sugiyama, EHP 92, 63 (1991); [2] P. Hemmerich and J. Lauterwein, Inorganic Biochemistry 1168 (1973)

MO 18.4 Thu 12:00 PH/SR106
Ultrafast coupling dynamics between the excited states of open chain carotenoids observed by fs time-resolved nonlinear vibrational spectroscopy — ●TAKESHI MIKI¹, RICHARD J. COGDELL², TIAGO BUCKUP¹, and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Institute of Biomedicine & Life Science, University of Glasgow, G12 8QQ Glasgow, Lanark, Scotland

The ultrafast femtochemistry of carotenoids is governed by the interaction between electronic excited states. Electronic dark states of carotenoids and their interaction with optically active S2 state have been suggested to play a major role in the ultrafast deactivation of carotenoids and its properties. Here, we investigate this interaction between such dark and bright electronic excited states of open chain carotenoids, particularly its dependence on the number of conjugated double bonds (N). We focus on the ultrafast wave packet motion on the modified potential surface by the interaction between bright and dark electronic states. Pump-degenerate four-wave mixing (pump-DFWM) is applied to a series of carotenoids with different number of conjugated double bonds N = 9, 10, 11 and 13. Our results indicate that short carotenoids display strongly distorted potentials when compared to longer carotenoids. The magnitude of this anharmonicity can be explained by the efficient coupling between S2 and a dark Sx state (in this case a Bu type), which stabilizes the higher energy levels of the C-C and C=C vibrational modes at early delay times (T < 50 fs).

MO 18.5 Thu 12:15 PH/SR106
Enantiomer Identification of Mixtures of Chiral Molecules with Broadband Microwave Spectroscopy — ●DAVID SCHMITZ¹, V. ALVIN SHUBERT¹, DAVID PATTERSON², JOHN M. DOYLE², and MELANIE SCHNELL¹ — ¹Max Planck Institute for the Structure and Dynamics of Matter at the Center for Free-Electron Laser Science, Hamburg, Germany — ²Department of Physics, Harvard University, Cambridge, MA, USA

Most molecules of biochemical relevance are chiral. Even though the physical properties of two enantiomers are nearly identical, they might exhibit completely different biological effects, e.g. one may be beneficial to health while the opposite is toxic. In nature and as products of chemical syntheses, chiral molecules often exist in mixtures with other chiral molecules. The analysis of these complex mixtures to identify the molecular components, determine which enantiomers are present, and to measure the enantiomeric excesses (ee) is still one of the challenging tasks of analytical chemistry.

We present here a new method of differentiating enantiomeric pairs of chiral molecules in the gas phase. It is based on broadband rotational spectroscopy and is a three-wave mixing process that involves a closed cycle of three rotational transitions. The phase of the acquired signal bears the signature of the enantiomer, as it depends upon the product of the three transition dipole moments. Furthermore, this technique allows for determining of the ee, which is proportional to the signal amplitude. Our technique can be applied to mixtures of chiral molecules, even when the molecules are very similar.

MO 18.6 Thu 12:30 PH/SR106
Matter-wave interference enhanced metrology on biomolecules — ●LUKAS MAIRHOFER, CHRISTIAN BRAND, PHILIPP GEYER, UGUR SEZER, LISA WÖRNER, and MARKUS ARNDT — Vienna University, Austria

Matter-wave interferometry is a powerful tool for the study of quantum properties of molecules (Berninger, PRA 76, 2007, Eibenberger, PRL 112, 2014). It has been demonstrated for up to 10.000 amu (Eibenberger, PCCP 15, 2013). As amplitude and phase of the fringe pattern are extremely sensitive to external forces matter-wave interference enhances the spatial resolution of deflectometry by a factor of 10⁴ compared to ballistic deflectometry. This has been successfully conducted for electric deflection (Eibenberger, NJP 13, 2011).

Thus matter-wave interferometry enhanced deflectometry makes high precision measurements on complex biomolecules feasible. The determination of their magnetic, electric and optical properties allows the investigation of their structure, of photo-induced conformational changes and of photochemistry in the gas phase. Additional water-bonds mimic the molecule's natural environment and allow us to study the transition from gas-phase to in-vivo-behaviour. We will present a geometry for deflection in magnetic fields suitable for interferometry which requires a homogenous force over the extension of the beam. Furthermore we will introduce a source for beams of internally cold, neutral and intact biomolecules up to 4000 amu that are sufficiently slow and intense for interference experiments. Finally we will report on recent progress in our research on biomolecules.

MO 18.7 Thu 12:45 PH/SR106

Valence-Shell-Photoelectron Imaging of Controlled Biomolecules — ●JOSS WIESE¹, SEBASTIAN TRIPPEL¹, and JOCHEN

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A molecule's chemical behaviour is governed by its electronic properties. Thus, a view at the evolution of the involved molecular orbitals during a reaction lures with insight into the fundamentals of chemistry.

In our experiments molecules are investigated by means of photoelectron imaging. State-selected molecular ensembles are laser aligned or mixed-field oriented inside a velocity map imaging spectrometer. The resulting velocity maps display the projected three dimensional distributions of both, the photoelectrons' kinetic energy and their release angle, in the molecular frame (MFPADs). MFPADs of various molecules will be discussed in terms of the molecular orbitals which are involved in the ionization process. Three dimensional MFPADs will be presented, which were obtained through tomographic reconstruction of the projected 2D images.