

MO 9: Biomolecules and Photochemistry

Time: Tuesday 14:30–16:30

Location: f102

Invited Talk

MO 9.1 Tue 14:30 f102
Structural investigations on a linear depsipeptide and cyclopeptides by combined IR/UV spectroscopy: Importance of dispersion interactions — ANKE STAMM, DOMINIC BERNHARD, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern

Depsipeptides as a special subclass of peptides contain at least one ester bond replacing a peptide bond which gives rise to a different folding behavior compared to an ordinary peptide. For a better understanding of their biological activity on a molecular level, knowledge on the structure of the isolated depsipeptides is of importance. As a first model system investigated in a molecular beam experiment we have chosen cyclohexylcarbonyl-glycine-lactate-2-anisidine (CyCO-Gly-Lac-NH-PhOMe; abbrev.MOC). MOC represents a linear depsipeptide whose structural investigation should give basic insights into preferred conformations of isolated depsipeptides. The system contains both an aromatic phenyl ring and an aliphatic cyclohexyl ring which interact via CH/ π dispersion interactions. This structure is only stable if dispersion is taken into account. An experimental analysis on the depsipeptide as well as on cyclopeptides is performed by application of mass- and isomer-selective combined double and triple resonance IR/UV methods in a molecular beam. In order to assign structures, DFT calculations including dispersion corrections were performed and compared with the experimental IR spectra.

MO 9.2 Tue 15:00 f102

Multiphoton microscopy for corneal pathologies diagnosis — ANA BATISTA^{1,2}, HANS GEORG BREUNIG^{1,3}, AISADA UCHUGONOVA¹, BERTHOLD SEITZ⁴, ANTÓNIO MIGUEL MORGADO^{2,5}, and KARSTEN KÖNIG^{1,3} — ¹Department of Biophotonics and Laser Technology, Saarbrücken, Germany — ²Institute for Biomedical Imaging and Life Sciences, Coimbra, Portugal — ³JenLab GmbH, Jena, Germany — ⁴Department of Ophthalmology, University of Saarland, Medical Center, Homburg/Saar, Germany — ⁵Department of Physics, Coimbra, Portugal

The diagnosis of corneal pathologies may be improved by multiphoton microscopy (MPM), which provides 3D imaging of the cornea with subcellular resolution, and information on tissue morphology and cells' metabolism. Here, we report on the use of MPM for ex-vivo characterization of non-pathological human corneas and evaluation of structural and metabolic changes due to pathology. A 5D multiphoton microscope with high spatial, temporal, and spectral resolutions was used for image acquisition.

All layers of the human cornea were characterized ex-vivo based on their autofluorescence and SHG. The autofluorescence lifetime of the metabolic co-factors NAD(P)H and flavins was used to assess the cells' metabolic state. Corneal samples with different pathologies showed significant differences in the metabolism of corneal epithelial cells. Different collagen fibrils structural organizations as well as autofluorescence lifetimes were observed in the corneal stroma of pathological samples. Discrimination between different pathologies was also feasible.

MO 9.3 Tue 15:15 f102

Time-resolved XUV photoelectron spectroscopy of organic molecules in solution — JOHAN HUMMERT, GEERT REITSMA, IASON KATECHIS, MARTIN ECKSTEIN, and OLEG KORNILOV — Max Born Institut Berlin, Germany

The characteristics and function of biologically relevant molecules are often controlled by their environment, i.e. an aqueous solution or a protein. To investigate this interaction it is therefore imperative to study electronic structure and dynamics of molecules in solution. For this purpose we implement time-resolved photoelectron spectroscopy which can provide information unaccessible with techniques like transient absorption spectroscopy.

We combine our time delay compensating XUV monochromator [1] with the liquid jet technique [2]. This enables us to probe molecular electronic states with a single XUV photon of tunable energy in the range of 10 to 50 eV. With a tunable excitation wavelength (TOPAS) and a demonstrated time resolution of 40 fs our setup is promising for investigation of diverse organic molecules in multiple solvents.

In first experiments we resolve the electronic ground states of wa-

ter soluble molecules, investigating the shift of the ionization potential due to solvation. We further observe changes of the photoelectron spectrum of liquid water upon exposure to 400 nm light.

[1] Eckstein et. al., JPCL 6, (2015): 419-25

[2] Faubel et. al., JCP 106, (1997): 9013-31

MO 9.4 Tue 15:30 f102

High-resolution study of the smallest sugar dimer: Interplay of hydrogen bonds in the glycolaldehyde dimer — SABRINA ZINN^{1,2,3}, CHRIS MEDCRAFT¹, THOMAS BETZ¹, 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 aggregation of glycolaldehyde was studied in a conformer-selective manner using high-resolution rotational spectroscopy in the gas-phase. Glycolaldehyde is formally the smallest sugar molecule, as it contains an aldehyde- and a hydroxy-group and was the first and so far the only sugar found in space. On this model system, we reveal hydrogen bond selectivity that guides the molecular recognition of carbohydrates in nature, in agreement with previous FTIR measurements.

In the high-resolution spectrum we assigned the rotational spectra of two stable dimer conformers. The lowest energy conformer reveals C_2 symmetry by forming two intermolecular hydrogen bonds and by giving up the rather strong intramolecular hydrogen bond. In addition, we assigned all of its singly ¹³C- and ¹⁸O- substituted species in natural abundance allowing us to determine the precise structure of this conformer. Predicting a precise structure of a weakly bound complex using quantum chemical calculations is still challenging, even for a small complex like the glycolaldehyde dimer. That is why an experimental determination of the structure is highly important to get precise information about the interplay of intermolecular interactions.

MO 9.5 Tue 15:45 f102

Molecular structure and chirality decrypted by rotational spectroscopy — SÉRGIO R. DOMINGOS¹, CRISTÓBAL PÉREZ¹, DAVID SCHMITZ¹, ANNA KRIN¹, AMANDA STEBER¹, DAVID PATTERSON², and MELANIE SCHNELL¹ — ¹Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany — ²Physics Department, Harvard University, Cambridge MA, United States

The ability to determine the conformation and handedness of chiral molecules is crucial in establishing how molecular structure and biological activity are related. Thus, fast and reliable methods that can analyze chiral mixtures are of utmost importance and are increasing in demand in chemical and pharmaceutical sciences. Chiral analysis using broadband rotational spectroscopy has been recently demonstrated [1] and is paving the way towards becoming an established analytical tool for chirality detection: radiation associated with a loop of three dipole-allowed rotational transitions is emitted exactly out of phase by molecules of opposite chirality, thus providing a direct signal of molecular chirality. The double-resonance scheme with two orthogonally-polarized transient electromagnetic fields results in the emission of microwave radiation along a third, mutually-orthogonal polarization, which we detect. The phase information encoded in the microwave field reveals the sign of the dipole-moment triple-product. Due to its resonant nature, microwave three-wave-mixing is developing into a probe of chirality with unprecedented conformer-selective capabilities. Recent studies on terpenes will be presented and discussed.

[1] Patterson D, Schnell M, Doyle JM, Nature 2013, 497, 475-477.

MO 9.6 Tue 16:00 f102

The Photodissociation of the Ortho-Xylyl Radical, C8H9, Investigated by Velocity Map Imaging — KAI PACHNER and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland Süd, 97074 Würzburg, Deutschland

Xylyl radicals can be found as intermediates in combustion processes. Their parent molecules, the xylenes, are used as additives in fuels to increase antiknock properties. The thermal decomposition of the xylyl radicals has been explored recently by Hemberger et al. in a synchrotron experiment [1]. Based on these studies, we investigated the photodissociation of the ortho-xylyl radical using velocity map imaging. Ortho-xylyl radicals were formed via flash pyrolysis in a pulsed

molecular beam using 2-methylphenethyl nitrite as a precursor. Irradiation of the ortho-xylyl radical with UV light leads to the formation of either ortho-xylylene or benzocyclobutene by hydrogen atom loss. Generated hydrogen fragments are then ionized in a [1+1']-REMPI process via the 1s-2p transition and detected on a velocity map imaging detector. The translational energy distribution of the hydrogen fragments as well as their angular distribution indicate a statistical dissociation for both pathways.

[1] Hemberger et al., J. Phys. Chem. A, 2014, 118, 3593 - 3604.

MO 9.7 Tue 16:15 f102

Tracking chemical reactions with time-resolved sulfur-1s spectroscopy: Light induced radical formation and isomerization of 4-Methylbenzenethiol in the liquid phase — MIGUEL OCHMANN¹, •INGA VON AHNEN¹, AMY CORDONES-HAHN², ABID HUSSAIN¹, JAE HYUK LEE², KIRYONG HONG^{2,3}, KATRIN ADAMCZYK¹, TAE KYU KIM³, ROBERT W. SCHONLEIN², ORIOL VENDRELL¹, and NILS HUSE¹ — ¹Department of Physics, University of Hamburg and

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Sulfur analogues to alcohols (R-SH) are abundant in nature and their chemistry is similar to alcohols. Recent results on the model system 4-methylbenzenethiol from transient absorption spectroscopy indicate sulfur radical generation upon UV excitation and formation of another species which eludes identification by optical spectroscopy. It was theorized that the hydrogen atom attaches to the aromatic ring. We used transient Sulfur-1s spectroscopy as a new element-specific probe of transient electronic and molecular structure. Two induced absorption peaks below the ground-state bleach clearly indicate formation of two new sulfur-species. Using TDDFT calculations we identified the thio-radical and a thione isomer with the photoejected hydrogen atom attached to the aromatic ring.