# MO 17: Biomolecules

Time: Wednesday 16:30–19:00 Location: F 142

MO 17.1 We 16:30 F 142

**Fluorescence Excitation and Emission Spectroscopy on an individual light harvesting complex 2 from *Rps. acidophila 10050*** — •Ralf Kunz[1], Kõu Timpmann[2], Arvi Freiberg[2], Richard J. Cogdell[3], and Jürgen Köhler[1] — [1]Experimental Physics IV, University of Bayreuth — [2]Institute of Physics, University of Tartu — [3]Molecular Biology, Faculty of Biomedical & Life Sciences, University of Glasgow

Low-temperature polarization dependent fluorescence-excitation spectra and fluorescence emission spectra are recorded from the same individual light harvesting 2 complexes from *Rps. acidophila strain 10050*. Combining fluorescence excitation and emission spectroscopy provides detailed information about the exciton band structure and the electron phonon coupling within these complexes. We have been able to identify the emission from the lowest exciton state ($k$=0).

MO 17.2 We 16:45 F 142

**Long-lived fluorescence of 1,6-Diphenyl-1,3,5-hexatriene** — •Katharina Hunger and Karl Kleinermanns — Heinrich-Heine-Universität, Düsseldorf, Deutschland

Carotines are an important molecule class for photosynthesis. They are part of the light-harvesting complex, with the task to absorb visible light and transfer the energy to the reaction center of the photosystem. All-trans-$\alpha$,$\omega$-diphenylpolyenes (also referred to as minicarotines) are well established model compounds for the bigger carotenoids such as $\beta$-carotene or lutein. Because of its favourable emission behaviour 1,6-diphenyl-1,3,5-hexatriene (DPH) is also used as fluorescence probe in biological membrane systems. The kinetic behaviour of the fluorescence of 1,6-diphenyl-1,3,5-hexatriene solution after excitation with a 355 nm laser pulse was observed in dependence of concentration and excitation pulse energy. Two mechanisms which cause fluorescence with different lifetimes compete. Below concentrations of 2.5 $\mu$M and excitation energies of 1 mJ only ordinary, short-lived fluorescence with a lifetime <20 ns is observed. Above this concentration and excitation energy, very intense and long-lived fluorescence is dominating. The lifetime of the emission can reach up to 70 ns and is decreased dramatically in presence of oxygen. We assume, that reverse intersystem crossing from the triplet state ladder repopulates the fluorescing S2 state after absorption of further photons in the triplet manifold.

MO 17.3 We 17:00 F 142

**Photostability of DNA building blocks** — •Laura Buschhaus[1], Katharina Hunger[1], Sergey A. Kovalenko[2], and Karl Kleinermanns[1] — [1]Heinrich-Heine-Universität, Düsseldorf, Deutschland — [2]Humbold Universität, Berlin, Deutschland

Guanosine monophosphate (GMP) solutions are studied with femtosecond and nanosecond broadband transient absorption spectroscopy. The sample was exited at 265 nm ($L_b$ / $L_a$ exitation) and 187 nm (solely $L_a$ exitation) and probed between 270-1000 nm with a temporal resolution of about 100 fs at different pH. Independent of the pH, the photoinduced evolution involves ultrafast $L_b$ - > $L_a$ conversion ($\tau << 100$ fs) and exhibits the presence of wide planar plateau on $L_a$. For neutral GMP a barrierless path connects this region to a conical intersection (CI) with the ground state, giving account of ultrafast decay of this species. For protonated $GMPH^+$ the system decays to a stable minimum characterized by out-of-plane displacement of NH and CH groups, which explains the longer (167 ps) fluorescence lifetime. $^1n_0\pi^*$ and $^1\pi\sigma^*$ states are predicted to play a less relevant role. GC Watson-Crick base pairs are studied with sub-ps to $\mu$s time resolution. It is shown that the short-time relaxation of the base pairs is dominated by internal relaxation of the G and C moieties while pair specific contributions like G ->C proton transfer play a less significant role. Instead in GG dimers electron transfer followed by proton transfer seems to take place and the electronic spectrum of the (G-H) radical is tentatively assigned.

MO 17.4 We 17:15 F 142

**Gas phase infrared spectra and corresponding DFT calculations of $\alpha$, $\omega$ diphenylpolyenes** — •Michaela Braun, Lars Biemann, and Karl Kleinermanns — Heinrich Heine Universität, Düsseldorf, Deutschland

Gas phase Fourier Transform InfraRed (FTIR) spectra of the homologue series of $\alpha$, $\omega$-diphenylpolyenes consisting of *trans*- and *cis*-stilbene, diphenylbutadiene (DPB) and diphenylhexatriene (DPH) are presented. These gas phase FTIR-spectra were obtained by a fast thermal heating technique that enables vaporization without decomposition. Infrared marker bands for the *cis*-isomers of the polyenes have been identified by density functional calculations at the B3LYP/TZVP level of theory. The measured infrared spectra are free from solvent effects and in very good agreement with the calculated vibrational frequencies. Furthermore, no indications for the thermal formation of DPB or DPH *cis*-isomers could be observed.

MO 17.5 We 17:30 F 142

**Aggregation of nucleosides in $CDCl_3$ studied by FTIR spectroscopy: From self-aggregation towards the Watson-Crick base pair** — •Lars Biemann[1], Thomas Häber[1], Klaus Schaper[2], and Karl Kleinermanns[1] — [1]Institut für Physikalische Chemie, Heinrich-Heine Universität, 40225 Düsseldorf — [2]Institut für Organische Chemie, Heinrich-Heine Universität, 40225 Düsseldorf

We reinvestigated the self-association of the nucleobase 1-cyclohexyluracil and of the nucleosides guanosine and cytidine in $CDCl_3$ solution and present the infrared spectra of their aggregates in the spectral regions between 1500 and 1800 $cm^{-1}$ and between 2700 and 3600 $cm^{-1}$. Applying a simple deconvolution procedure to a series of infrared spectra measured at different concentrations allows for a separation of the contributions of monomers and clusters. This method has successfully been applied to adenine and does not require a restriction of the size of the aggregates. On this basis, wavelength dependent absolute extinction coefficients of the uracil monomer and dimers could be extracted. Comparison of the deconvoluted dimer spectra with quantum chemical calculations allows for a structural assignment of the dimer structures that coexist in solution. Extending this analysis to the guanosine-cytidine system allows for the examination of the formation of larger aggregates beyond the dimer and elucidates the question wether the Watson-Crick GC base pair is predominant in $CDCl_3$ solution.

MO 17.6 We 17:45 F 142

**Direct Determination of Milk Fat Content Using Raman Spectroscopy** — •Rasha Hassanein, Pinkie Eravuchira, Patrice Donfack, Bernd von der Kammer, and Arnulf Materny — Jacobs University Bremen, Bremen, Germany

The composition of milk is an important factor in dairy industry. Specifically, fat protein and carbohydrate are of interest, since these components have to be labeled on milk and milk products; they are used as an indicator for milk quality. Among all mentioned components milk fat content plays a significant role for consumers and dairy industry such as butter producer. Many different approaches have been considered as official methods for the determination of the fat content. These traditional methods are time consuming or need a special treatment of the milk with chemicals. A fast online analysis technique would be on the demand of the industry. Raman spectroscopy has already been successfully applied to food analysis. Due to the fingerprint characteristics of the Raman spectra, they are useful for the analysis of different components. In our presentation, we introduce Raman spectroscopy in combination with chemometric analysis as a rapid, straightforward and nondestructive tool for the quantification of fat content in liquid homogenized milk. Additionally, we show that using Raman spectroscopy is capable of determining the unsaturation level of milk fat. The results are in each case compared to the results of standard techniques.

MO 17.7 We 18:00 F 142

**Microhydration of two polyalanine-based peptides** — •Sucismita Chutia, Mariana Rossi, Volker Blum, and Matthias Scheffler — Fritz Haber Institute, Berlin, Germany

Microsolvation studies using vibrational spectroscopy are an important approach for analysing the influence of the solvent environment on peptides. Two small peptides have been the subject of such experimental studies in the recent years: Ac-$Ala_5$-$LysH^+$ [1] and Ac-Phe-$Ala_5$-$LysH^+$ [2]. The aim of this work is to theoretically identify the lowest-energy conformers of these peptides and carry out microhydration studies to find the preferred water binding sites. We first use a

molecular dynamics calculation with the OPLS-AA force-field potential in the TINKER package to scan the potential energy surface for a wide variety of candidate conformers. We then use the all-electron electronic structure code *FHI-aims* [3] to follow up these structures with van der Waals corrected density functional theory to determine the energy hierarchy, and vibrational frequencies for comparison with the experimental spectra. Our findings indicate that both helical and "non-helical" conformers are present among the low-energy conformers of Ac-Phe-Ala5-LysH+, similar to the case of Ac-Ala5-LysH+. We find that, for both Ac-Phe-$Ala_5$-$LysH^+$ and Ac-$Ala_5$-$LysH^+$, the water molecule binds to the protonated lysine end in the lowest energy conformer. We also address the accuracy of the pre-screening forcefield compared to DFT-vdW. [1] M. Kohtani and M.F.Jarrold, *JACS*, **126**, 8454-8458 (2004) [2] J.A. Stearns *et al*, *PCCP*, **11**, 125-132 (2009) [3] V. Blum *et al*, Comp. Phys. Comm. **180**, 2175 (2009).

MO 17.8 We 18:15 F 142

**Simultaneous observation of ultrafast ligand dissociation and docking-site trapping in heme proteins using upconversion infrared spectroscopy** — •Patrick Nuernberger, Kevin F. Lee, Adeline Bonvalet, Marten H. Vos, and Manuel Joffre — Laboratoire d'Optique et Biosciences, Ecole Polytechnique, Centre National de la Recherche Scientifique, 91128 Palaiseau, France, and Institut National de la Santé et de la Recherche Médicale, U696, 91128 Palaiseau, France

We report on ultrafast visible pump/mid-infrared probe spectroscopy of the carboxy form of heme proteins by employing the recently developed chirped-pulse upconversion technique, which allows both high resolution and sensitivity over an extremely broad spectral range. Commonly, the bleach signal due to ligand dissociation and the incipient docking-site absorption signal, being about 200 $cm^{-1}$ apart and differing by more than an order of magnitude in absorptivity, are studied individually. We here monitor them simultaneously, allowing a direct observation and a concurrent analysis of the initial processes after photoinduced ligand dissociation, for instance the formation of hot vibrational bands.

MO 17.9 We 18:30 F 142

**Isolation of charged (bio)molecules in liquid helium nanodroplets** — •Frauke Bierau, Peter Kupser, Gerard Meijer, and Gert von Helden — Fritz-Haber-Institut, D-14195 Berlin, Germany

Superfluid helium droplets provide an isothermal ultracold environment for embedded molecules and are ideal matrices for optical spectroscopy [1].

We set up an experiment, which provides a facility to perform (vibrational) spectroscopy on ultracold mass-selected biomolecules in helium droplets. Proteins or peptides are brought into the gas phase via electrospray ionization (ESI), are stored in a linear ion trap and picked up by helium droplets.

We have seen that molecular ions as big as Cytochrome C ($\simeq$12kDa) can be incorporated in He droplets and are detectable as an electrical current on a copper plate. The He droplet masses were determined by electrostatic deflection in an electrical field between two plates, whereupon the deflection angle was measured as a function of the charge state of an embedded Cytochrome C ion. It turned out that the He droplets are real massive and composed of more than $10^{10}$ He atoms per droplet under the initial expansion source parameters [2] of 30 bar and 8K. After being picked up, the cold dopant molecules can be irradiated by a counter-propagating laser beam, and spectroscopic experiments can be performed. [1] J. P. Toennies, A. F. Vilesov, Angew. Chem. Int. Ed. 2004, 43, 2622, [2] H. Buchenau et al., J. Chem. Phys. 1990, 92, 6875

MO 17.10 We 18:45 F 142

**(Un)folding polyalanines: probing high-temperature stability from first principles** — •Mariana Rossi, Volker Blum, Alex Tkatchenko, and Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin

Peptides in vacuo offer a unique, well-defined testbed to match experiments directly against first-principles approaches that predict the intramolecular interactions that govern peptide and protein folding. In this respect, the polyalanine-based peptide Ac-$Ala_{15}$-$LysH^+$ is particularly interesting, as it is experimentally known to form helices in vacuo, with stable secondary structure up to $\sim$750 K [1]. Room-temperature folding and unfolding timescales are usually not accessible by direct first-principles simulations, but this high $T$ scale allows a rare *ab initio* view. We here use van der Waals (vdW) corrected [2] density functional theory in the PBE generalized gradient approximation as implemented in the all-electron code FHI-aims [3] to show by Born-Oppenheimer *ab initio* molecular dynamics that Ac-$Ala_{15}$-$LysH^+$ indeed unfolds rapidly (within a few ps) at $T$=800 K and 1000 K, but not at 500 K. We show that the structural stability of the $\alpha$ helix at 500 K is critically linked to a correct vdW treatment, and an interplay of the designed $LysH^+$ ionic termination and vdW is essential for the observed helical secondary structure. [1] M. Kohtani *et al.*, JACS **126**, 7420 (2004). [2]A. Tkatchenko, M. Scheffler, PRL **102**, 073005 (2009). [3] V. Blum *et al.*, Comp. Phys. Comm. **180**, 2175 (2009).