MO 2: Biology Related Molecules

Time: Monday 10:30–12:30 Location: PA 1.150

MO 2.1 Mon 10:30 PA 1.150

Repelling and Ordering: The Influence of PEG on Protein Adsorption — •Christoph Bernhard[1], Steven J. Roeters[2], Johannes Franz[1], Tobias Weidner[1,2], Mischa Bonn[1], and Grazia Gonella[1] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Aarhus University, Aarhus, Denmark

Nanoparticles and liposomes can be used as versatile drug nanocarriers. Upon injection into the bloodstream a protein layer will immediately coat the nanocarrier surface. This alteration of the surface chemistry can induce changes of the drug carrier properties and interfere with the carrier's targeting mechanism. In order to prevent this non-specific protein adsorption the drug nanocarriers are often coated with a protein repelling PEG layer. However, recently, it has been shown that the adsorption of certain proteins can be beneficial and promote specific cellular uptake. Therefore, a deeper understanding of protein adsorption to PEGylated surfaces is desirable to control the protein corona composition. Here we use mixed lipid monolayers consisting of DMPE and DMPE-PEG2000 as model systems for PEGylated surfaces. We study the influence of interactions between the lipid head groups and the proteins as well as steric repulsion from the PEG chains on the adsorption behavior of bovine serum albumin and fibrinogen. Surface sensitive vibrational sum-frequency generation spectroscopy is used to probe the orientation and structure of the proteins at the lipid/water interface. Our results suggest that an increasing PEG density not only influences the amount of adsorbed proteins, but in the case of Fibrinogen also the ordering at the surface.

MO 2.2 Mon 10:45 PA 1.150

In-Depth Investigation of the Aggregation Process of Insulin with Time-Resolved Fluorescence Studies — •Bastian Geissler, Dirk Wesberg, and Patrick Nuernberger — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

The quaternary structure of proteins can be essential for a certain functionality. On the contrary, misfolded proteins can cause cellular dysfunction and are suspected to determine degenerative diseases like Parkinson's or Alzheimer's disease. Misfolded proteins autocatalytically form insoluble amyloid fibrils, which are commonly known as plaques. The formation of fibrils can be observed with marker dyes like Thioflavin T (ThT) whose fluorescence yield increases during the process due to the modified surrounding. In this study, we employ ThT and measure the aggregation of insulin fibrils using time-resolved fluorescence, either by time-correlated single-photon counting or by a streak camera, and with pulsed excitation alternately at 375 or 405 nm in order to excite different sub-ensembles of the ThT molecules. Whereas the process itself takes hours, we monitor not only the fluorescence yield but also how the lifetimes and emission spectra of ThT change during fibril formation. Since the latter two aspects are associated with the geometry of ThT, we obtain insight into the binding situation of ThT to the fibrils and during the fibril formation.

MO 2.3 Mon 11:00 PA 1.150

Photorelaxation of Uracil in Explicit Biological Environments — •Sebastian Reiter, Daniel Keefer, and Regina de Vivie-Riedle — Department of Chemistry, LMU Munich

Ultraviolet radiation can trigger photochemical reactions in nucleic acids that might result in damage to the genetic code. Such processes are however largely prevented by the intrinsic property of the five canonical nucleobases to dissipate the absorbed energy via ultrafast, non-radiative relaxation pathways. So far, these processes have been investigated mostly on isolated nucleobases in the gas phase. In this context, recent studies elucidate the relaxation process of uracil after optical excitation to the bright S_2 state ($\pi\pi^*$) with femtosecond laser pulses [1, 2]. In our present theoretical work, we go beyond gas phase simulations and investigate uracil in its native RNA environment, where the sugar-phosphate backbone and neighboring nucleobases as well as solvent molecules might influence the relaxation pathway. For this purpose, we employ an approach that combines wave packet dynamics with molecular dynamics [3] to study the ultrafast population decay from the S_2 excited state through a conical intersection to S_1, while explicitly taking environmental effects into account. We present our multiscale methodology and discuss the influence of different combinations of neighboring nucleobases and surrounding water molecules on the photostability of uracil.

[1] S. Matsika *et al.*, *J. Phys. Chem. A*, **117**, 12796 (2013).
[2] D. Keefer *et al.*, *J. Am. Chem. Soc.*, **139**, 5061 (2017).
[3] S. Thallmair *et al.*, *J. Chem. Theory Comput.*, **11**, 1987 (2015).

MO 2.4 Mon 11:15 PA 1.150

Ultrafast Photoinduced Ring Closing in Photoswitchable Diarylethene-Based Nucleosides — •Jose Luis Perez Lustres[1], Yang Li[1], Hans Robert Volpp[1], Tiago Buckup[1], Theresa Kolmar[2], Andres Jaeschke[2], and Marcus Motzkus[1] — [1]PCI, Universität Heidelberg, Germany — [2]IPMB, Universität Heidelberg, Germany

Diarylethene-based nucleosides are novel photoswitchable compounds, where the nucleobase forms the core of the molecular switch.(1) The latter undergoes ring closing/opening reactions upon conrotatory movement of the side chains. The process is reversible and occurs on ultrafast timescales with high yield.(2) Thus, these DNA building blocks are designed to control and report about DNA structure. We address here the ring closing reaction by broadband fs transient absorption in the near UV. The signature of the closed structure is detected in the sub picosecond timescale. Transient anisotropy indicates strong structural reorganisation occurring in the course of vibrational relaxation. Finally, spectral analysis of the non-decaying component demonstrates branching at the earliest stages of the photoreaction. The analysis is facilitated by a novel strategy to isolate the absorption coefficients of the open and closed forms from steady-state UV–Vis absorption spectra obtained during long time irradiation at selected wavelengths.

1. Cahova, H.; Jaeschke, A., *Angew Chem Int Edit* **2013**, *52 (11)*, 3186-3190.
2. Buckup, T.; Sarter, Ch.; Volpp, H.-R.; Jaeschke, A.; Motzkus, M., *J. Phys. Chem. Lett.* **2015**, *6*, 4717-4721.

MO 2.5 Mon 11:30 PA 1.150

UV-Induced Self-Repair of a DNA Lesion Traced with Quantum Chemistry — •Daniel Keefer, Vitus Besel, and Regina de Vivie-Riedle — Department of Chemistry, LMU Munich

Nucleobases in DNA and RNA absorb UV light, which can lead to several interesting photophysical and photochemical processes. In a recent experimental study [1], it was revealed that photoexcitation of a guanine (G) adenine (A) sequence can even lead to self-repair of an adjacent cyclobutane pyrimidine dimer (CPD) lesion in oligonucleotides. The proposed mechanism involves photoexcitation of G at 290 nm, followed by a long-living charge transfer state between G and A and subsequent electron donation from the A radical anion to the CPD lesion. This finally induces ring splitting and repair of the damaged nucleobase sequence.

In our theoretical study, we use (multiscale) quantum chemical methods in order to verify this mechanism. The excited states of the GA sequence adjacent to the CPD lesion are computed using high-level active space methods, including explicit consideration of the residual oligonucleotide and the water environment. We will discuss the existance and accessibility of G $\rightarrow$ A charge transfer states, and trace the time evolution of the experimentally addressed states in the system after photoexcitation by means of semiclassical dynamics.

[1] D. Bucher et al. *J. Am. Chem. Soc.* 2016 **138**, 186.

MO 2.6 Mon 11:45 PA 1.150

Rotational dynamics of indole(H_2O) dimer clusters — •Linda V. Thesing[1], Andrey Yachmenev[1,2], Rosario González-Férez[3], and Jochen Küpper[1,2,4] — [1]Center for Free-Electron Laser Science, DESY, Hamburg, Germany — [2]Center for Ultrafast Imaging, Universität Hamburg, Germany — [3]Instituto Carlos I, Universidad de Granada, Spain — [4]Department of Physics, Universität Hamburg, Germany

We present a time-dependent study of the rotational dynamics of a non-rigid molecule in combined ac and dc fields. We compute the alignment and orientation dynamics of the prototypical indole(H_2O) dimer, including the coupling of the overall rotation to the internal rotation of the water moiety and compare our results to calculations treating the indole(H_2O) clusters as rigid molecules. We show that due to the small coupling between the rotational and torsional motions, the

rigid rotor approximation can be employed for typical field strengths in alignment and orientation experiments. Furthermore, by varying the dependence of the polarizability and electric dipole moment on the torsional angle as well as increasing the external field strengths, we explore regimes where the internal rotation of the water molecule affects the rotational dynamics of the full indole(H_2O) cluster. We estimate that for laser intensities larger than 10^{13} W/cm^2 the influence of the internal rotation of the water molecule can no longer be neglected.

MO 2.7 Mon 12:00 PA 1.150

Rotationally Resolved Electronic Stark Spectroscopy of 3-Cyanoindole and the 3-Cyanoindole-water Complex — •Michael Schneider, Marie-Luise Hebestreit, Christian Henrichs, and Michael Schmitt — Insitute for Physical Chemistry I, Heinrich-Heine-Universität, Düsseldorf, Germany

The electronic origin of 3-cyanoindole has been investigated using high resolution laser induced fluorescence spectroscopy (HRLIF) to analyze its electronic nature. By means of evolutionary algorithms, molecular parameters like the rotational constants in the electronic ground and first excited state and the orientation of the transition dipole moment were determined. To investigate the permanent dipole moments in the ground and first excited state a homogeneous static electric field was applied, which lifts the M degeneracy by the Stark effect and results in band splittings and shifts.

To understand how solvation influences the electronic nature of the excited state, the binary 3-cyanoindole water cluster was investigated. The different molecular parameters were used to assign the band to optimized CC2-pVTZ structures by comparing the experimental and calculated *ab initio* values.

MO 2.8 Mon 12:15 PA 1.150

Spatially separated conformers of the dipeptide Ac-Phe-Cys-NH_2 — •Nicole Teschmit[1,2,3], Karol Długołęcki[1], Daniel Gusa[1], Igor Rubinsky[1], Daniel A. Horke[1,2], and Jochen Küpper[1,2,3,4] — [1]Center for Free-Electron Laser Science, DESY, Hamburg, Germany — [2]The Hamburg Center for Ultrafast Imaging, Universität Hamburg, Germany — [3]Department of Chemistry, Universität Hamburg, Germany — [4]Department of Physics, Universität Hamburg, Germany

The conformational separation of biomolecules in the gas phase is an important step toward atomic-resolution diffraction experiments, attosecond dynamics experiments, or kinetic studies of the chemical reactivity of a single conformer.

Here, we present the combination of a laser desorption (LD) source for the vaporization of labile biological molecules [1] with electrostatic control for the spatial separation of conformers [2]. We now demonstrate the conformer separation of the prototypical peptide Ac-Phe-Cys-NH_2. We detail the characterization and optimization of LD beams, the use of strong field ionization as an universal probe, and the preparation of conformer-pure beams of the Ac-Phe-Cys-NH_2 dipeptide. We analyze options for diffractive imaging of these controlled samples.

[1] N. Teschmit, K. Długołęcki, D. Gusa, I. Rubinsky, D. A. Horke, J. Küpper, J. Chem. Phys. 147, 144204 (2017)

[2] Y.-P. Chang, D. A. Horke, S. Trippel, J. Küpper, Int. Rev. Phys. Chem. 34, 557 (2015)