MO 1: Biomolecules

Time: Monday 10:30–13:00 Location: TOE 317

MO 1.1 Mon 10:30 TOE 317

Two-photon fluorescence excitation (TPF) spectroscopy of photosynthetic pigments and pigment-protein complexes — •Alexander Betke[1], Bernd Voigt[1], Heiko Lokstein[2], and Ralf Menzel[1] — [1]Institut für Physik und Astronomie / Photonik, Univ. Potsdam — [2]Institut für Biochemie und Biologie, Univ. Potsdam

Chlorophylls and carotenoids are light-harvesting pigments and essential structural components of photosynthetic pigment-protein complexes. Due to the optically forbidden character of the lowest excited singlet state ($S_1/2^1A_g^-$) of relevant carotenoids for one-photon excitation from the electronic ground state ($S_0/1^1A_g^-$), the relative energy position of the carotenoid S_1 state cannot be readily investigated by conventional spectroscopic techniques. This state, however, was generally assumed to be at least partly involved into excitation energy transfer to adjacent chlorophyll molecules, based on its supposed close energetic proximity to the chlorophyll S_1 (Q_y) state. The carotenoid S_0- to S_1-transition is two-photon allowed and consequently individual spectral peaks in the TPF spectra (detected by chlorophyll fluorescence) of several light-harvesting complexes are usually ascribed to this transition. However, from direct comparison to TPF spectra of relevant chlorophylls in solution we infer that there is no effective energy transfer from the carotenoid $2^1A_g^-$ state onto chlorophyll Q_y. We conducted TPF studies with the plant major light-harvesting complex and chlorophylls in solution. In particular we discuss the progression of chlorophyll states in TPF spectra, which is considerably different from that in one-photon absorption or -fluorescence excitation spectra.

MO 1.2 Mon 10:45 TOE 317

A computational study of polyalanine-based peptides and their microsolvation — •Sucismita Chutia, Mariana Rossi, Volker Blum, and Matthias Scheffler — Fritz Haber Institute, Berlin, Germany

Microsolvation is an important method to map the transition of isolated gas-phase peptides to their fully solvated states. In our study, we aim to theoretically identify the lowest energy conformers, the preferred water binding sites, and the influence of water molecules on the structure of two small peptides previously studied in *vacuo* experiments, Ac-Ala$_5$-LysH$^+$[1] and Ac-Phe-Ala$_5$-LysH$^+$[2]. A basin hopping search with the OPLS-AA force-field in TINKER followed by calculations with the all-electron electronic structure code FHI-aims [3] using the van der Waals corrected [4] PBE density functional is used to determine the low energy conformers. We find both pure and mixed helices among the lowest energy structures of the non-hydrated peptides. During microsolvation, the first water molecule prefers to bind to the protonated lysine end. The subsequent water molecules tend to cluster around the protonated end as well as the carbonyl group. As the number of discrete water molecules increase, a different "more solvated" structure becomes the global minimum. *Ab initio* molecular dynamics is used to study the stability of some of these structures when fully solvated with explicit solvent molecules. [1] M. Kohtani and M. F. Jarrold, *JACS*, **126**, 8454(2004)[2] J.A. Stearns et al., *PCCP*, **11**,125(2009) [3] V. Blum et al., *Comp.Phys.Comm.*, **180**, 2175 (2009)[4] A. Tkatchenko and M. Scheffler, *PRL*, **102**, 073005 (2009)

MO 1.3 Mon 11:00 TOE 317

Catching Proteins in Liquid Helium Droplets — •Frank Filsinger, Frauke Bierau, Peter Kupser, Gerard Meijer, and Gert von Helden — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Superfluid helium droplets provide an isothermal ultracold environment for embedded molecules and are ideal matrices for optical spectroscopy [1]. Recently, we set up a new experiment to dope He droplets with biomolecular ions [2]. In this approach, biomolecules are brought into the gas phase via electrospray ionization (ESI) and are selected according to their mass-to-charge ratio in a quadrupole mass spectrometer. The ions are then stored in a linear ion trap, from which they are picked up by a pulsed beam of helium droplets. While in the initial experiments very large He droplets (composed of 10^{10}-10^{12} atoms) were observed [2], a new He droplet source enables us now to embed amino acids, peptides, and even small proteins in droplets consisting of 10^4 to 10^6 He atoms depending on the dopant molecules. We will discuss how the size of the doped droplets can be directly measured by accelerating the doped droplets in an electric field. Furthermore, we will present our progress towards IR spectroscopy of these cold biomolecular ions.

[1] J. P. Toennies, A. F. Vilesov, Angew. Chem. Int. Ed. **43**, 2622 (2004) [2] F. Bierau et al., Phys. Rev. Lett. **105**, 133402 (2010)

MO 1.4 Mon 11:15 TOE 317

Coarse graining protein motion: FIRST/FRODA and normal modes of motion. Can theory meet experiment? — •J Emilio Jimenez-Roldan[1,2], Stephen A Wells[1], Robert B Freedman[2], and Rudolf A Röemer[1] — [1]Dept. Physics, Centre for Scientific Computing, University of Warwick, Coventry, CV4 7AL U.K. — [2]Life Sciences, Coventry, University of Warwick, CV4 7AL, U.K.

We explore the conformational change of Protein Disulphide Isomerase using Rigid Cluster Decomposition constraints and Normal Modes of Motion. Our simulations show that the active sites of the protein are able to move within a range over 40 Angstroms for one of the directions of motion. In order to test these results we carry out polyactylamide gel electrophoresis experiments using cross-linkers of different lengths that bind to the active sites to identify the minimum length between the active sites. Our simulations are based on first, the coarse graining model criteria defined by FIRST software which is able to identify flexible and constrainted regions, and second, on Normal Modes of Motion which map out the directions of motion for a given network. Using the FRODA module, together with the coarse graining constrains given by FIRST and Normal Modes of Motion we identify large scale conformational changes at low computational cost.

MO 1.5 Mon 11:30 TOE 317

First-principles study of the conformational space of the NTA His-tag anchoring system for peptide force spectroscopy — •Franziska Schubert, Volker Blum, and Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin

For intramolecular force measurements with atomic force microscopy (AFM) a universal anchor system to grab and release the protein of interest is of high relevance [1]. The Ni-NTA His-tag has been proposed as a candidate for such an anchor. In recent years, there have been many experimental studies to analyze the stability and reversibility of the bond between Ni-NTA and Histidine tagged proteins [2]. In our theoretial analysis of the conformational space of the NTA His-tag, we performed prescreenings of the potential energy surface in the gas-phase with the OPLS-AA force field potential in the Tinker package. On top of that we use density functional theory with a generalized-gradient functional (PBE) corrected for van der Waals interactions [3] as implemented in the all-electron code FHI-aims [4] to identify the energy hierarchy and lowest conformers. While in a vacuum environment binding to only one imidazole ring is preferred for unprotonated NTA-Ni, the second bond is closed when NTA is protonated or the molecule is solvated in water. To understand the screening mechanisms enhancing the stability of the Ni-imidazole bond, we also investigate the solvation of the molecule in chloroform for different protonation states of NTA. [1] L. Schmitt et al., Biophys. J. 78, 3275 (2000), [2] C. Verbelen et al., J. Mol. Recognit. 20, 490-494 (2007), [3] A. Tkatchenko et al., PRL 102, 7 (2009), [4] V. Blum et al., Comp. Phys. Comm. 180, 2175 (2009)

MO 1.6 Mon 11:45 TOE 317

IR spectra of microhydrated acetanilide cluster cations — •Matthias Schmies[1], Alexander Patzer[1], Kohei Tanabe[2], Mitsuhiko Miyazaki[2], Masaaki Fujii[2], and Otto Dopfer[1] — [1]Optik und Atomare Physik, TU Berlin, Germany — [2]Chemical Resources Laboratory, Tokyo Institute of Technology, Japan

Acetanilide is one of the simplest aromatic molecules featuring a -NH-CO- peptide bond. We present IR photodissociation spectra of mass-selected complexes of the acetanilide cation microsolvated by a controlled number of ligands (L=argon, molecular nitrogen, and water). The IR spectra are analyzed by comparison with DFT calculations (M06-2X/aug-cc-pVTZ) and provide detailed information about the interaction potential (ligand binding site and interaction energy) between this prototypical biomolecular building block and polar/nonpolar ligands. Whereas Ar and molecular nitrogen preferentially bind to the aromatic ring, water exhibits hydrogen bonding to

the acidic NH group of the amide moiety. The current work shows that ionization of acetanilide has a large effect on its charge distribution and its interaction with hydrophilic and hydrophobic ligands. In particular, the hydration environment is largely affected by the change in the charge distribution.

MO 1.7 Mon 12:00 TOE 317

Ab initio calculation of interactions of Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} with 19 amino acids — •Matti Ropo, Volker Blum, and Matthias Scheffler — Fritz Haber Institut der Max-Planck-Gesellschaft, Berlin, Germany

Ca has a very important role in cellular signaling in all organisms; cytoplasmic concentrations are typically very low, so when present it acts to trigger various signaling. Unfortunately, heavy metals like Pb can potentially disturb Ca dependent functions[1]. In this study, we investigate the interactions of Ca, Sr, Ba, Cd, Pb and Hg ions with 19 different amino acids in vacuo, using accurate *ab initio* calculations based on density functional theory (DFT) and the van der Waals [2] corrected PBE functional. The conformational search was performed using a force-field based (OPLS-AA) basin hopping search [3], followed by all-electron DFT calculations[4] for a wide range of conformers. For each amino acid, we considered at the outset three different types of termination: uncharged termination (-NH2/-COOH), zwitterionic, and capped with acetyl(ace)/N-Methyl-Amide(nma) groups. The database reveals trends such as: the zwitterionic conformation is preferred over normal almost in all amino acids with Ca ion; the strongest binding energies for Ca are found with ace/nma caps; Ca binds most strongly to arginine; Pb bind uniformly stronger than Ca. [1]H.A. Godwin, Curr.Opin.Chem.Biol. **5**, 223 (2001) [2]A. Tkatchenko and M. Scheffler, Phys.Rev.Lett. **102**, 73005 (2009) [3]J.W. Ponder,TINKER 5.1; Washington Univ. School of Medicine, Saint Louis, MO (2009) [4]V. Blum *et al.*, Comp.Phys.Comm. **180**, 2175 (2009).

MO 1.8 Mon 12:15 TOE 317

Onset of α-helical preference on gas-phase Ac-Ala$_n$-LysH$^+$: insights from *ab initio* theory — •Mariana Rossi, Volker Blum, Xinguo Ren, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Faradayweg 4-5, D-14195, Berlin

The smallest size of polypeptides to form helices in the gas phase can be matched between theory and experiment, and brings us essential information about the intrinsic stability of this well-known secondary structure motif. For the case of the alanine-based Ac-Ala$_n$-LysH$^+$ series in the gas phase, indirect measurements from single water adsorption experiments[1] have indicated helix onset at n=8. We here focus on determining quantitatively, based on density-functional theory (DFT), the structural and energetic properties of exactly this series. Starting from a force field conformational screening, we fully relax more than 1000 conformers using the van der Waals (vdW) corrected[2] PBE exchange-correlation (xc) potential. α-helical preference is found to start between n=7-8, in agreement with experiment, but only if vdW interactions are taken into account. For a few of the lowest energy conformers for n=4-8, we test different vdW corrected xc functionals and benchmark our results against explicitly correlated methods, by developing and using a numeric atom-centered basis set which allows us to converge energy differences. Finally, the qualitatively different energetic contributions (H-bonds, vdW, electrostatics) for this helix onset are dissected, explaining the stability of these structures. [1] Kohtani and Jarrold, JACS 108, 8454 (2004); [2] Tkatchenko and Scheffler, PRL 102, 073055 (2009)

MO 1.9 Mon 12:30 TOE 317

The impact of Li^+ ions on the conformation of the prolyl-peptide bond — •Carsten Baldauf, Volker Blum, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Proline has a special role amongst the canonical amino acids. Within a peptide chain, the stabilities of the cis and trans state of the prolyl-peptide bond are very similar, but they are separated by a high barrier. Prolyl-cis-trans isomerization is under discussion as molecular timer for protein (re)folding. Li^+ ions can change the cis/trans ratio of model peptides.[1,2] We here present a comparative study of the impact of the monovalent cations Li^+ and Na^+ on the conformation of the model peptide Ac-AlaAlaProAla-NMe (AAPA). The conformational space of the system is pre-screened with a force field-based sampling approach and further refined with density functional theory (DFT) calculations for a wide range of the minima found. We observe drastic discrepancies between energy hierarchies from popular force fields and from DFT (van der Waals corrected PBE functional),[3] demonstrating that both Li^+ and Na^+ must be treated much more carefully than with a simple force field to assess their true role in shaping peptide conformations. Li^+ can induce a ribbon-like conformation of AAPA without H-bonding but stabilized by cations bridging between backbone carbonyl oxygens.

[1] Reimer U et al. J Mol Biol. 1998; 279:449. [2] Kofron JL et al. Biochemistry. 1991; 30:6127. [3] Tkatchenko A, Scheffler M. Phys Rev Lett. 2009; 102:073005.

MO 1.10 Mon 12:45 TOE 317

Femtolysis – Investigation of biological relevant molecules by femtosecond lasers coupled to a FT-ICR mass spectrometer — •Christian Neidel[1], Andreas Kühn[2], Frank Noack[1], Claus Peter Schulz[1], Ingolf V. Hertel[1], and Michael Linscheid[2] — [1]Max Born Institute, Max-Born-Str. 2a, 12489 Berlin — [2]Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

First experiment on the combination of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with intense femtosecond laser pulses will be reported. By means of the strong laser field fragmention and sequencing of large biomolecules like DNA and proteins was introduced and detected with high mass resolution provided by this type of mass spectrometer. Results for several different molecular model systems will be presented. These type of experiments provide a new approach to study protein sequencing and fragmentation of, e.g., messenger molecules and pollutants.