

MO 2: Biomoleküle 1

Zeit: Montag 14:00–16:00

Raum: VMP 6 HS-F

MO 2.1 Mo 14:00 VMP 6 HS-F
IR/UV double resonance spectroscopy on reactive isolated molecules in the S_1 and T_1 states — ●KRISTINA BARTL, ANDREAS FUNK, and MARKUS GERHARDS — Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern

Photochemical reactions are of great interest due to their importance in chemical and biological processes. IR/UV double and triple resonance spectroscopy in molecular beam experiments in combination with *ab initio* and DFT calculations yields information on reaction coordinates and Intersystem Crossing (ISC) processes subsequent to photoexcitation. We present the first applications of combined IR/UV spectroscopy on reactive isolated molecules and triplet states in molecular beams without using any messenger molecules. In the case of 3-hydroxyflavone the IR spectrum subsequent to an excited state proton transfer has been recorded. However, photoinduced reactions involve not only singlet but also triplet states. As an archetype molecule xanthone is analysed. After excitation to the S_2 state, ISC occurs into the triplet manifold leading to a population of the T_1 state. The IR spectrum of the T_1 state has been recorded for the first time using the UV/IR/UV technique. The experimentally obtained vibrational transitions fit ideally to the calculated frequencies (DFT, B3LYP functional, TZVP basis) of the T_1 state.

MO 2.2 Mo 14:15 VMP 6 HS-F
IR/UV investigations on an isolated cyclic tetrapeptide and its clusters with water — ●KIRSTEN SCHWING¹, STEFAN KUBIK², and MARKUS GERHARDS¹ — ¹Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern — ²Organische Chemie, TU Kaiserslautern

Cyclopeptides are a widespread class of substances in nature with the antibiotic valinomycin being one the most famous representatives. Their physiological effects are frequently based on the tendency to form bioactive conformations. Therefore the investigation of their structure is of great importance for understanding their functionalities. The mass-, isomer- and state-selective IR/R2PI spectroscopy represents an ideal tool for the structural investigation on isolated molecules in the gas phase. With the help of this spectroscopic method the cyclic tetrapeptide (Pro-Tyr)₂ and its clusters with water are investigated. In combination with DFT calculations we are able to perform structural assignments for the electronic ground state of the cyclopeptide. Furthermore structural suggestions for the mono- and dihydrated clusters are presented.

MO 2.3 Mo 14:30 VMP 6 HS-F
Ac-Ala_nLysH⁺ in vacuo: secondary structure of polyaniline peptides part I — ●FRAUKE BIERAU, PETER KUPSER, GERT VON HELDEN, MARIANA ROSSI, VOLKER BLUM, MATTHIAS SCHEFFLER, and GERARD MEIJER — Fritz-Haber-Institut, D-14195 Berlin, Germany

For peptides and proteins, IR vibrational spectroscopy on modes that are sensitive to hydrogen bonding is one of the key techniques to investigate the conformational structure. When studying molecules in the gas phase, IR spectra can provide information about intrinsic intramolecular properties, without intermolecular interactions with the environment being present [1].

Polyalanine chains can serve as model systems for helical peptides in the gas phase [2]. IR multiple photon dissociation (IR-MPD) spectroscopy at T= 300 K is performed on Ac-Ala_nLysH⁺ (n=5,10,15,19) polypeptides in the spectral range between 1000 and 2000 cm⁻¹, where the amide I (C=O stretching vibration) and amide II (N-H bending vibration) bands are located. The peptides are brought into the gas phase via electrospray ionization (ESI), isolated in a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer and irradiated by the free-electron laser FELIX, and the wavelength-dependent change of mass-to-charge is recorded. For the amide I band, a red-shift with increasing chain length is observed. This is in agreement with DFT calculations (part II).

[1] Special issue "Bioactive molecules in the gas phase", PCCP 6 (2004), 2543-2890, [2] Hudgins et al., JACS 120 (1998), 12974.

MO 2.4 Mo 14:45 VMP 6 HS-F
Ac-Ala_nLysH⁺ in vacuo: secondary structure of polyaniline

peptides part II (Density Functional Theory) — ●MARIANA ROSSI, VOLKER BLUM, PETER KUPSER, GERT VON HELDEN, FRAUKE BIERAU, GERARD MEIJER, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Predicting the structure and stability of peptides is a challenge, and *in vacuo* studies provide unique, well-defined conditions to match state-of-the-art experiments and theory. We here present a combined force field (OPLS) / density-functional theory (DFT) study of the polyaniline peptides Ac-Ala_nLysH⁺ (n=5,10,15), for which earlier experiments indicate helical secondary structure [1]; the results are verified by comparing to room-temperature multiphoton IR vibrational spectra measured using the FELIX free-electron laser (part I). For Ac-Ala₅LysH⁺, we pre-screen O(10⁵) candidate structures in the force field, and then use DFT in the generalized gradient approximation with van der Waals corrections (GGA+vdW) in the FHI-aims code [2] to refine a wide range of low-energy conformers. We show (i) how the LysH⁺ termination acts to stabilize helical structures, and (ii) a close energetic competition between different helical motifs (e.g. α , 3_{10} , mixed) in the Ala₅ part. The vibrational spectra are consistent with an α -helical motif. We address systematic frequency shifts between theoretical (harmonic) and the measured spectra, and the role of anharmonicity through extensive *ab initio* molecular dynamics simulations. [1] R. Hudgins, *et al.*, JACS 120, 12974 (1998). [2] V. Blum, *et al.*, Comput. Phys. Comm., accepted (2008).

MO 2.5 Mo 15:00 VMP 6 HS-F
Light-harvesting complexes in a membrane environment: A time-resolved fluorescence study — ●TOBIAS PFLOCK¹, FLORIAN SPREITLER¹, JUNE SOUTHALL², RICHARD COGDELL², JÜRGEN KÖHLER¹, and SILKE OELLERICH¹ — ¹Experimentalphysik IV, Universität Bayreuth, D-95447 Bayreuth — ²Glasgow Biomedical Research Centre, University of Glasgow, UK

Picosecond time-resolved fluorescence spectroscopy has been used to investigate the intercomplex energy-transfer properties of membrane-reconstituted light-harvesting 2 (LH2) complexes from the purple bacteria *Rhodospseudomonas acidophila*. LH2 complexes were reconstituted in phospholipid model membranes at different lipid-protein ratios and all samples were excited with a wide range of excitation densities and excitation rates.

In order to explain the fluorescence decay data, we use a nonlinear decay model. This model takes annihilation of excitation into account, which is interpreted as a signature of self-organized clustering of the LH2 complexes within the lipid bilayer environment. This conclusion is corroborated by AFM data.

MO 2.6 Mo 15:15 VMP 6 HS-F
Energietransfer B800-B850 in mutierten LH2-Antennenkomplexen — ●THOMAS BRUST¹, SIMONE DRAXLER¹, ANDREA RAUH¹, MARTINA V. SILBER², PAULA BRAUN², WOLFGANG ZINTH¹ und MARKUS BRAUN¹ — ¹Lehrstuhl für BioMolekulare Optik, Fakultät für Physik, LMU München — ²Biozentrum der LMU München

Photosynthese ist die Umwandlung von solarer in chemisch speicherbare Energie. Die primären Schritte in dieser langen Reaktionskette sind das Einfangen und Weiterleiten der Energie. Hierbei sind die Antennenkomplexe LH2 von Purpurbakterien eines der am besten untersuchten Systeme.

In diesem Beitrag wird der Energietransfer zwischen den Bakteriochlorophyllringen (BChl) B800 und B850 des LH2 in Abhängigkeit von Mutationen innerhalb der Proteinbindungstasche des Purpurbakteriums *Rhodobacter sphaeroides* mittels stationärer und transienter Absorptionsspektroskopie untersucht. Die Energietransferzeit variiert zwischen 0,7 ps (Wildtyp) und 1,0 ps [1]. Die spektroskopischen Eigenschaften der B850-Absorptionsbande hängen ebenfalls von der Mutation ab. Die beobachteten Korrelationen der Energietransferzeit mit der Lage, Breite und Intensität der B850-Bande deuten an, dass die Mutationen strukturelle Unordnung und veränderte Besetzungen in den Ringen B800 und B850 hervorrufen. Dadurch werden die Interaktionen zwischen den BChl-Molekülen beeinflusst und die funktionellen Eigenschaften der LH2-Antennenkomplexe verändert.

[1] T. Brust et al., Chem. Phys. (2008), doi:10.1016/j.chemphys.2008.08.007

MO 2.7 Mo 15:30 VMP 6 HS-F

Design Criteria for Optimal Photosynthetic Energy Conversion — •BENJAMIN FINGERHUT¹, WOLFGANG ZINTH², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie and Biochemie, Ludwig-Maximilians-Universität München, 81377 München, Germany — ²Institut für BioMolekulare Optik, Ludwig-Maximilians-Universität München, 80538 München, Germany

Photochemical solar energy conversion is considered as an alternative of clean energy. For future light converting nano-machines photosynthetic reaction centers are used as prototypes optimized during evolution. We introduce a reaction scheme for global optimization and simulate the initial, ultrafast charge separation in photochemical energy conversion [1]. Multiple molecular charge carriers are involved in this process and are linked by Marcus-type electron transfer. In combination with evolutionary algorithms, we unravel the biological strategies for high quantum efficiency in photosynthetic reaction centers and extend these concepts to the design of artificial photochemical devices for energy conversion.

The generalization of the model to the detailed balance limit together with multi-objective optimization allows to deduce an upper limit for the efficiency of photochemical solar energy conversion and a direct comparison to semiconductor based systems.

[1] B. P. Fingerhut, W. Zinth and R. de Vivie-Riedle, Chem. Phys. Lett. *466*, 209 (2008).

MO 2.8 Mo 15:45 VMP 6 HS-F

Quantitative detection of cholesterol in stratum corneum model systems by coherent anti-Stokes Raman scattering microscopy — •GREGOR HEHL¹, ALEXANDER KOVALEV², PATINCHARATH NANDAKUMAR³, and ANDREAS VOLKMER¹ — ¹3rd Institute of Physics, University of Stuttgart, Stuttgart, Germany — ²MPI für Metallforschung, Stuttgart, Germany — ³Physics Department, Birla Institute of Technology and Science, Pilani-Goa, India

We report on the hyperspectral coherent anti-Stokes Raman scattering (CARS) imaging of lipids in stratum corneum, the top most barrier on the epidermis that prevents the penetration of external reagents through the skin. Investigations are carried out on mixtures consisting of ceramide, stearic acid and cholesterol, the three main lipid species of stratum corneum. Multiplex CARS microspectroscopy [1] is used for spatially and frequency resolved spectroscopic measurements with sub-micron and 5 cm⁻¹ resolution, respectively. The reconstruction of linear Raman spectra from recorded multiplex CARS spectra is achieved by phase retrieval using the Maximum Entropy method [2]. Based on the characteristic Raman bands of cholesterol, ceramide and stearic acid in the C=C and C-H stretch region, we demonstrate the quantitative determination of the respective species concentrations, and the formation of cholesterol-rich domain structures in the electroporated stratum corneum model system.

[1] A. Volkmer, J. Phys. D: Appl. Phys. *38* (2005), R59-R81

[2] E. Vartiainen, K.-E. Peiponen, T. Asakura, Appl. Spectrosc. *50* (1996), 1283-1289