MO 11: Biomolecules

Zeit: Montag 14:00–16:00 Raum: 6B

MO 11.1 Mo 14:00 6B

IR/UV-double resonance spectroscopy of electronically excited flavonoids — •Kristina Bartl[1], Holger Fricke[1], Kirsten Schwing[1,2], Andreas Funk[1], and Markus Gerhards[1,2] — [1]H.-Heine Universität Düsseldorf, Institut für Physikalische Chemie I, 40225 Düsseldorf — [2]TU Kaiserslautern, Fachbereich Chemie, 67663 Kaiserslautern

Flavonoids are well known for their antioxidative effect. Spectroscopically, flavonoids like 3-hydroxyflavone or 5-hydroxyflavone are of special interest, since a keto-enol-tautomerism takes place after electronic excitation. In order to obtain detailed structural information on the reaction coordinate, combined IR/UV-spectroscopy is applied on electronically excited states in a mass selective molecular beam experiment: In a first step an isomer selective resonant excitation in different electronically excited states is performed and the IR-spectra of these excited states are analyzed by resonant IR-excitation followed by UV-ionisation. By comparison with the isomer selective IR-spectra of the ground state (obtained by another combined IR/UV method) and in combination with ab initio and DFT calculations, structural changes can be identified in detail. Not only the structure sensitive coordinates of the OH and C=O stretching vibrations but also the whole IR spectrum up to the upper fingerprint region can be analyzed by using a newly developed IR laser system. In this presentation investigations of different hydroxyflavones, starting with 3-hydroxyflavone and its clusters with water are presented. Different isomers as well as reaction coordinates are discussed.

MO 11.2 Mo 14:15 6B

The Photophysics of 10-Methylisoalloxazine: A Quantum Chemical Investigation — •Susanne Salzmann and Christel Marian — Institute of Theoretical Chemistry and SFB663, Heinrich Heine Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany

In recent years flavins have recieved growing attention due to their decisive role as cofactors in phototropins. In the LOV (light, oxygen, and voltage sensitive) domain of the blue light receptor the primary step after light absorption involves a rapid decay of the excited singlet state to the lowest excited triplet state via an intersystem crossing (ISC) mechanism. In aqueous solution, the free flavin shows a different behaviour, the ISC efficiency decreases and the fluorescence increases in comparison to the LOV domain.

Vertical and adiabatic electronic spectra of 10-methylisoalloxazine have been investigated by means of combined density functional and multi-reference configuration interaction methods. Spectral shifts due to electrostatic interactions in aqueous solution are taken into account employing the conductor-like screening model. Spin-orbit interaction has been computed involving a nonempirical mean-field approach. On the basis of these calculations, we suggest that in the LOV domain the ISC takes place between the excited $^1(\pi \rightarrow \pi^*)$ state (S_1) and the $^3(n \rightarrow \pi^*)$ state (T_2). In aqueous solution this ISC channel is not accessible due to the blue shift of the $^3(n \rightarrow \pi^*)$ state.

MO 11.3 Mo 14:30 6B

Excitation Energy Transfer via Optically "Dark" States of Carotenoids in Photosynthetic Antenna Complexes investigated by Femtosecond Two-Photon Fluorescence Exciatation Spectroscopy — •Alexander Betke[1], Bernd Voigt[1], Heiko Lokstein[2], and Ralf Menzel[1] — [1]Institut für Physik, Lehrstuhl für Photonik, Universität Potsdam — [2]Institut für Biochemie und Biologie, Universität Potsdam

Carotenoids play several important roles in photosynthetic organisms: as integral structural components of pigment-protein-complexes, as light-harvesting pigments, and in photoprotection.
To study the last two mentioned functions and the underlying mechanism(s) it is vital to know the energetic positions of the lowest-lying excited singlet state, S_1 ($2^1A_g^-$) of relevant carotenoids. The latter states are assumed to be close to the (bacterio-)chlorophyll S_1 state. Due to their "optically forbidden" character, the carotenoid S_1 state is difficult to investigate by conventional one-photon spectroscopy. However, the $1^1A_g^-$ to $2^1A_g^-$ transition is strongly two-photon allowed. Thus, simultaneous two-photon absorption of tuneable femtosecond near infrared pulses monitored by (bacterio-) chlorophyll fluorescence is a powerful approach to study the role of these "dark" states in excitation energy transfer and dissipation in light-harvesting complexes. We will present recent results obtained with different light-harvesting complexes and highlight advantages as well as possible pitfalls of this approach.
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MO 11.4 Mo 14:45 6B

Elektronentransfer im photosynthetischen Reaktionszentrum: Optimierung in Modell und Natur — •Benjamin Fingerhut[1], Wolfgang Zinth[2] und Regina de Vivie-Riedle[1] — [1]Department Chemie, LMU, Butenandtstr. 11, 81377 München — [2]BMO, Sektion Physik, LMU, Oettingenstr. 67, 80538 München

Die Photosynthese als wichtigster Energiekonversionsschritt in der belebten Natur wurde im Zuge der Evolution über viele Jahrmillionen optimiert. Für ein verbessertes Verständnis dieser Vorgänge wurde ein theoretisches Modellsystem entwickelt, in dem der photosynthetische Elektronentransfer im bakteriellen Reaktionszentrum nachgebaut wurde. Das Simulationssystem berücksichtigt die wichtigsten Randbedingungen des Proteins. Mit Hilfe eines genetischen Algorithmus wurden relevante Parameter der mehrstufigen Transferkette optimiert. Die Untersuchungen zeigen die Bedeutung der verschiedenen molekularen Parameter für die Funktion des Reaktionszentrums. Die im Optimierungsprozess gefundenen Parametersätze werden mit aus Experimenten bekannten Informationen verglichen und zeigen für einen vorgegebenen Organismus in wesentlichen Bereichen eine gute Übereinstimmung. Das Auftreten von optimalen Parameterkonstellationen die nicht in der Natur realisiert sind wurde untersucht.

MO 11.5 Mo 15:00 6B

Towards the structure-selective measurement of exited state dynamics in DNA clusters — •Yuliya Rulyk[1], Elena Samoylova[1], Thomas Schultz[1], Hans-Hermann Ritze[1], Wolfgang Radloff[1], and Ingolf-Volker Hertel[1,2] — [1]Max Born Institute, Max-Born Strasse 2a, D-12489, Berlin, Germany — [2]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195, Berlin, Germany

Femtosecond pump-probe mass and electron spectroscopy is a powerful method for studying ultrafast exited state relaxation in DNA clusters. Nevertheless, this method has two substantial limitations. First, it is not selective with respect to different isomers of DNA clusters, which are expected to show different exited state dynamics. Second, the investigation of small clusters is impeded by fragmentation of bigger clusters.

To overcome the limitations mentioned, we develop an advanced method which combines ns hole-burning spectroscopy and time-resolved fs pump-probe mass spectroscopy. In this experiment, selected species are ionized by a ns UV pulse and removed from the active region of a spectrometer. The remaining species are characterized with fs pump-probe mass spectroscopy. We report on the progress and a first test of the experiment on indole-water clusters.

MO 11.6 Mo 15:15 6B

X-ray photoelectron spectroscopy of amino acids in aqueous solution — •Dirk Nolting[1], Manfred Faubel[2], Ingolf-Volker Hertel[1], and Bernd Winter[1] — [1]Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Deutschland — [2]Max-Planck-Institut für Dynamik und Selbstorganisation, Göttingen, Deutschland

The effect of solvation and protonation on the N 1s and C 1s core levels of amino acids was studied. For this a water beam was injected into a vacuum chamber and crossed with a synchrotron radiation beam. By varying the pH of the solution, different charge states could be addressed which made it possible to study protonation effects on nitrogen and adjacent carbons. Protonation caused a shift of 2 eV of N 1s to higher binding energies and a significantly smaller shift of 0.3 eV to adjacent carbon atoms.

MO 11.7 Mo 15:30 6B

Enantiomeric dependence of the THz spectra of polycrystalline Tyrosine and Valine — •Konstanze Schröck[1], Alan B. True[2], Timothy A. French[2], Martina Havenith[1], and Charles

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We used Terahertz Time-Domain Spectroscopy (THz TDS) to investigate the far-infrared absorption features of the two amino acids tyrosine and valine. The THz radiation was generated on a ZnTe(110) crystal by a regeneratively amplified Ti:Sapphire laser (repetition rate of 1 kHz, wavelength of 800 nm, 100 fs pulses with an energy of 1 mJ). The polycrystalline samples were pressed into pellets with a thickness of 0.25-0.5 mm. They were placed in a cryostat and spectra were taken under vacuum at room temperature and at 77 K. Furthermore, a temperature-dependent study of valine in the range of 77 to 290 K was undertaken. The absorption spectra of both the D and L enantiomers, as well as the DL racemates in the range of 0.1 to 2.5 THz will be presented. We show that the vibrational spectra of the D and L enantiomers are identical, but differ from the racemic mixtures. For all samples, the absorption maxima were found to be red-shifted as a function of increasing temperature. Furthermore, a computational study (CHARMM) was used to identify the molecular motions observed in the spectra. The vibrational modes are more intermolecular than intramolecular in character due to the hydrogen-bonding network.

MO 11.8 Mo 15:45 6B

PH Enhancement on the Adsorption Reaction of Nanodiamond/Nanosilica and Lysozyme Molecule — •Victor Wei-Keh Wu — Department of Chemical and Material Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan — Group 510, Institute of Atomic and Molecular Sciences, Academia Sinica, P.O.Box 23-166, 10617 Taipei, Taiwan — Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, 33602 Bielefeld, Germany, Email:victorbres3tw@yahoo.com.tw, http://www.che.kuas.edu.tw

Fluorescences from free lysozyme of 0-1000 nM in 7 mM PPBS at pH = 7, 9, 11 and 13 after adsorption reactions on the surfaces of nanodiamond/-silica (d≈100 nm, 5 μg/2.02 mL) with Xe lamp as light source monochromated at 285 nm of ca. 0.6 mW and PMA-11 of Hamamatsu as fluorescence spectrometer have been measured. Coverages as well as adsorption reaction constants (e.g. 1.6 x 10^8/4.5 x 10^7 $[nM]^{-1}$ for nanodiamond/-silica, respectively, at pH = 11) have been further obtained. Their quotients for both systems at pH = 7 - 13 is ca. 4. The max. appears at around 11 - 13, where lysozyme as "neutral" (pI≈11.5) can be easierly adsorbed. The available surface areas of nanodiamond and -silica during adsorption for each lysozyme can be estimated as 10 and 2 nm^2, respectively. Comparing this ratio with the quotients of the measured adsorption reaction constants, roughness of particle surface may also be decisive besides charge on and modification of the surface, pH of the surrounding for higher adsorption capability. The adsorbed lysozyme on the surface of nanodiamond may better keep its helicity as well as its activity. **Ref.** V. W.-K. Wu, Chem. Lett. 35, 1380 (2006)