MO 1: Biomoleküle

Zeit: Montag 14:00–16:00 Raum: 3F

Hauptvortrag MO 1.1 Mo 14:00 3F

Ultrafast Dynamics of Non-Radiative Processes in Electronically Excited DNA Building Blocks — •Friedrich Temps and Nina K. Schwalb — Institut für Physikalische Chemie, Universität Kiel, D-24098 Kiel

In a thrust to shed light on the mechanisms responsible for the high UV photostability of DNA, we study the electronic relaxation dynamics of free nucleobases, selected hydrogen-bonded base pairs, and short single- and double-stranded oligonucleotides using femtosecond fluorescence spectroscopy. Recent new results concern the modified base N^6N^6-dimethyladenine, which shows so-called "dual fluorescence". Time-resolved measurements after excitation at different wavelength, starting just above the electronic origin, showed that the observed red-shifted emission previously ascribed to an intramolecular charge transfer state arises virtually without time delay. By comparison with adenine, it is suggested that the optically excited state undergoes a transformation through a conical intersection to a relaxed excited state, which is responsible for the red fluorescence and may be related to the $\pi\pi^*(L_b)$ or the $n\pi^*$ state. In addition, time-resolved fluorescence decay data will be reported for guanosine-cytidine (G·C) Watson-Crick base pairs in solution. The results demonstrate a strong acceleration of the radiationless electronic relaxation in G·C compared to the free monomers. Excitation wavelength and solvent dependent measurements resolved the gas vs. solution phase puzzle, where apparently different behaviors were observed. Eventually, an outlook is given on experiments on short DNA chains with different sequences.

MO 1.2 Mo 14:30 3F

Structural Assignment of Adenine Aggregates in $CDCl_3$ — •Lars Biemann[1], Thomas Häber[1], Daniela Maydt[2], Klaus Schaper[2], and Karl Kleinermanns[1] — [1]Institut für Physikalische Chemie, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany — [2]Institut für Organische Chemie, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany

We reinvestigated the self-association of 9-substituted adenine derivatives in $CDCl_3$ solutions and present the infrared spectra of 9-ethyladenine and N-methyl-9-ethyladenine and its aggregates in the spectral regions between 1500 and 1800 cm^{-1} and between 2700 and 3600 cm^{-1}. Wavelength dependent absolute extinction coefficients of the monomer and dimers are presented on the basis of a simple deconvolution method. Comparison of the deconvoluted dimer spectra with quantum chemical calculations allows for a structural assignment of the two dimer structures that coexist in 9-ethyladenine/$CDCl_3$ solutions. In contrast, the dimer spectrum of N-methyl-9-ethyladenine is dominated by a single isomer.

MO 1.3 Mo 14:45 3F

IR/UV-double resonance spectroscopy of 3-hydroxyflavone and its aggregates with water — •Kristina Bartl, Andreas Funk, Holger Fricke, Kirsten Schwing, and Markus Gerhards — TU Kaiserslautern, Fachbereich Chemie, Schrödingerstr. 52, 67663 Kaiserslautern & H.-Heine Uni Düsseldorf, Institut für Physikalische Chemie I, 40225 Düsseldorf

Flavonoids are well known for their antioxidative and photoprotective effects. Spectroscopically 3-hydroxyflavone is of special interest, as a keto-enol-tautomerism takes place after electronic excitation. In order to obtain structural information about 3-hydroxyflavone and its aggregates with water, IR laser spectroscopy from the fingerprint region to the OH stretching modes is a very powerful tool especially in combination with UV spectroscopy and mass spectrometry leading to the isomer selective IR/R2PI [infrared/ resonant 2-photon ionisation] method. We show that the application of this method to the electronically excited states yield in combination with ab initio calculations direct information on the structure and reaction coordinates. For the aggregates with water different isomers have to be considered and it is the strength of this technique that a structure can unambiguously be assigned according to the IR spectra of the excited states. Thus we are able to answer the open question if proton transfer takes place in the aggregates after electronic excitation.

MO 1.4 Mo 15:00 3F

Investigation of Optically "Dark" Excited States of Carotenoids by Femtosecond Two-Photon Excitation Spectroscopy — •Alexander Betke[1], Bernd Voigt[1], Heiko Lokstein[2], and Ralf Menzel[1] — [1]Institut für Physik/Photonik, Universität Potsdam, Am Neuen Palais 10, D-14415 Potsdam, Germany — [2]Institut für Biochemie und Biologie, Universität Potsdam, Karl- Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany

Carotenoids are essential components of pigment-protein-complexes in photosynthetic organisms: they are important for structural stability, serve as accessory light-harvesting pigments and protect the photosynthetic apparatus from photo-oxidative damage. The carotenoid lowest excited singlet state S_1 ($2^1A_g^-$) is assumed to be relevant for the latter two functions. For a study of the underlying mechanisms a proper knowledge of its energetic position would be necessary. However, single photon transitions between the carotenoid ground state S_0 ($1^1A_g^-$) and this state are symmetry-forbidden and thus, its investigation by conventional spectroscopy is hampered. On the other hand the S_0-S_1-transition is two-photon allowed, which makes two-photon absorption a suiteable approach for an investigation of the carotenoid S_1 energies. We present near-infrared femtosecond laser two-photon excitation spectra of light-harvesting antenna-complexes with different carotenoid complements and discuss implications for excitation energy transfer and photoprotective mechanisms.
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MO 1.5 Mo 15:15 3F

Comparison of the fluorescence kinetics of detergent-solubilized and membrane-reconstituted LH2 complexes — •Tobias Pflock[1], Manuela Dezi[2], Giovanni Venturoli[2], Richard J. Cogdell[3], Jürgen Köhler[1], and Silke Oellerich[1] — [1]Experimentalphysik IV, Universität Bayreuth, D-95447 Bayreuth — [2]Dept. of Biology, University of Bologna, Italy — [3]GBRC, University of Glasgow, UK

Picosecond time-resolved fluorescence spectroscopy has been used in order to compare the fluorescence kinetics of detergent-solubilized and membrane-reconstituted light-harvesting 2 (LH2) complexes from the bacteria Rhodopseudomonas (Rps.) acidophila and Rhodobacter (Rb.) sphaeroides. LH2 complexes were reconstituted in phospholipid model membranes at different lipid:protein-ratios and all samples were studied exciting with a wide range of excitation densities. While the detergent-solubilized LH2 complexes from Rps. acidophila showed monoexponential decay kinetics ($\tau_f = 980$ ps) for excitation densities of up to $3\cdot10^{13}$ photons/(pulse·cm^2), the membrane-reconstituted LH2 complexes showed multiexponential kinetics even at low excitation densities and high lipid:protein-ratios. The latter finding indicates an efficient clustering of LH2 complexes in the phospholipid membranes. Similar results were obtained for the LH2 complexes from Rb. sphaeroides.

MO 1.6 Mo 15:30 3F

Raman Spectroscopic Investigation of the Influence of Biological Rhythms on Bone Composition of Hamsters — •Jing Shen[1,2], Jiming Hu[2], Alexander Lerchl[1], and Arnulf Materny[1] — [1]Jacobs University Bremen, Germany — [2]Wuhan University, China

Biological rhythms regulate the lives of mammals. It has been reported that changes of the photoperiod result in variations of the melatonin synthesis and sequential changes of body weight, fur color and gonadal function in Djungarian hamsters [1]. Since the hormone level acts as a regulator for the metabolism of bone, certain changes in the bone composition have to be expected. In our study, Raman spectroscopy was applied to observe the differences in bones comparing long- (16L:8D) and short-day (8L:16D) photoperiod Djungarian hamsters. Recently, Raman spectroscopy has been widely used in biology and medicine due to its capability to analyze different bio-components. The method provides information about inorganic component-calcium compounds and organic component-collagen in bone at the same time. Our results show that LD cortical bone samples possess a higher phosphate-to-carbonate ratio in both femur and tibia. It is assumed that the metabolism of the bone is influenced by hormones such as gonadotrophin and melatonin, which are produced in varying amounts during the different photoperiods.
[1] A. Lerchl *et al.*, *Neuroendocrinology* **57**,359 (1993).

MO 1.7 Mo 15:45 3F

Raman Spectroscopy for the Characterization of Animal Tissue — Toward Molecular Monitoring of Tumorigenicity and Hormonal Changes — •Patrice Donfack[1], Jing Shen[1,2], Alexander Lerchl[1], and Arnulf Materny[1] — [1]Jacobs University Bremen, Germany — [2]Wuhan University, China

Current investigation methods of biological systems are mostly based on time-demanding immunoassays and histopathological examination of sample biopsies. The availability of rapid *in-situ* techniques would be of great advantage. A potential candidate is Raman spectroscopy (RS), which provides specific molecular fingerprints in a non-invasive and non-destructive way. In our contribution we present two examples for an application of RS for the investigation of animal tissue. (i) Hamsters are strongly influenced by seasonal changes of day and night ratio. Experiments on metabolic or hormonal changes in hamsters unequally exposed to daylight have resulted in changes in the Raman spectra of spleen and liver tissue. (ii) RS was also performed to characterize biomolecular alterations in cells of AKR mice predisposed to leukemia. The Raman spectra of AKR mice spleen tissues show a prominent contribution of the β-sheet conformation, which can be unambiguously assigned to the protein's amide I band. The intensity ratios of this amide I band and the CH2-deformation line at 1450 cm^{-1} was found to be different for cancerous and healthy mice. Clear changes could also be observed for the nucleic acid band at approx. 1085 cm^{-1} and *e.g.* for a double band at 1606 and 1635 cm^{-1}.