MO 16: Biomoleküle

Zeit: Dienstag 14:00–19:00 Raum: Poster C1

MO 16.1 Di 14:00 Poster C1

Raman Spectroscopy Discrimination of HaCaT and A5RT3 Human Skin Model Cell Lines — •Patrice Donfack, Maren Rehders, Klaudia Brix, and Arnulf Materny — Jacobs University Bremen, Germany

HaCaT and its tumorigenic counterpart A5RT3 cell lines represent good models for studying human skin keratinocytes and carcinoma derived from them. Traditional detection methods of tumor cells relying on immunoblotting are time-consuming. Optical methods are potentially much faster. Fluorescence imaging focuses on the characterization of already known differentiation or dedifferentiation markers. However, Raman spectroscopy (RS) is capable of yielding fingerprint-like characterization of the sample without the necessity of restricting the analysis to few molecules of interest. In our contribution we show the application of RS and surface enhanced RS (SERS) to distinguish between normal HaCaT and tumorigenic A5RT3 cells. Striking differences were revealed in the overall Raman intensity as well as the intensity ratio of the protein amide I band at 1657 and the CH_2 deformation band at 1447 cm^{-1}. These changes were even further pronounced in the SERS experiments. Lipids are more effective Raman scatterers than proteins. The relatively stronger enhancement of the CH_2 deformation band points to a significantly different lipid content in HaCaT. Furthermore, A5RT3 cells showed higher nucleus/cytoplasm ratios with prominent DNA vibrations and a higher but partly altered protein contribution indicating modifications of cellular metabolism and differentiation state.

MO 16.2 Di 14:00 Poster C1

Single-molecule spectroscopy on low-light adapted light-harvesting 2 complexes of *Rhodopseudomonas palustris* — •Paul Böhm[1], Tatas Brotosudarmo[2], Silke Oellerich[1], Richard Cogdell[2], and Jürgen Köhler[1] — [1]Experimental Physics IV and Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth — [2]Division of Biochemistry and Molecular Biology, Institute of Biomedical and Life Sciences, Biomedical Research Building, University of Glasgow

Low temperature (1.4 K) single-molecule fluorescence-excitation spectra have been recorded for a novel low-light (LL) adapted light-harvesting 2 (LH2) complex from *Rhodopseudomonas palustris*. For bulk samples the main spectroscopic feature of this complex in the near infrared is a ratio of 2.9 between the absorption maxima at 800 nm and 850 nm. All studied individual complexes feature 2-3 broad absorption bands in the 840-870 nm spectral region revealing a characteristic polarization dependence. In the 800 nm region the spectra of the individual complexes show several narrow absorption lines which vary from complex to complex both with respect to the number of lines and spectral positions. These measurements may contribute to the elucidation of the electronic structure of this novel light-harvesting complex, as to the narrow lines in the 800 nm region could indicate localized excitations on one or a few B800 bacteriochlorophyll *a* molecules, whereas the broad bands in the 850 nm region may suggest that the excitations are delocalized over a large number of B850 bacteriochlorophyll *a* molecules.

MO 16.3 Di 14:00 Poster C1

Pigment-Pigment Interactions in Light-Harvesting Complexes Investigated by Nonlinear Laser Spectroscopy — •Alexander Betke[1], Bernd Voigt[1], Roger G. Hiller[2], Maria Krikunova[3], Heiko Lokstein[4], and Ralf Menzel[1] — [1]Institut für Physik/Photonik, Universität Potsdam, Germany — [2]Macquarie University, School of Biological Sciences, Australia — [3]Institut für Experimentalphysik, Universität Hamburg, Germany — [4]Institut für Biochemie und Biologie, Universität Potsdam, Germany

Two-photon fluorescence excitation- and nonlinear polarization spectroscopy in the frequency domain (NLPF) are sensitive methods to study pigment-pigment interactions in photosynthetic light-harvesting complexes (LHCs). Among the studied complexes are the peridinin-chlorophyll *a* - protein (PCP) and higher plant LHC II. Interactions between the peridinins and peridinin-chlorophyll interactions in PCP are resolved in the NLPF spectra. Excitonic interactions between the peridinins are revealed. Certain peridinin(s) show interaction between their "optically dark" S_1 ($2^1A_g^-$) or intramolecular charge-transfer state and chlorophyll *a*. Thus, these states are approximately isoenergetic. Two-photon absorption of zeaxanthin and violaxanthin in LHC II monitored by chlorophyll fluorescence shows spectral differences of their "optically dark" $2^1A_g^-$ states. Specific changes in xanthophyll-chlorophyll interactions upon aggregation of LHC II are indicated by NLPF. These changes may underlay the chlorophyll-fluorescence quenching as the molecular basis of excess energy dissipation. Consequences for energy transfer in these complexes are discussed. Supported by the SFB 429.

MO 16.4 Di 14:00 Poster C1

Ion-induced radiation damage to DNA-building blocks — Fresia Alvarado, Jos Postma, Sadia Bari, Przemek Sobocinski, Ronnie Hoekstra, and •Thomas Schlathölter — KVI Atomic Physics, University of Groningen, The Netherlands

The interaction of keV protons and heavy ions with DNA building blocks is of particular biological relevance in view of the increasing number of facilities employing MeV proton/heavy-ion irradiation for tumor treatment. When these ions traverse tissue and are decelerated to sub MeV energies, the so-called Bragg-peak is reached where the induced damage is highest due to maximum linear energy transfer (LET) and relative biological effectiveness (RBE) at these energies. Biological consequences of irradiation with energetic protons and heavy ions from galactic cosmic rays (GCR) and solar particle events (SPE) are also a limiting factor for human space exploration.

We investigate the response of isolated DNA building blocks and their clusters upon keV singly and multiply charged ion impact using high resolution coincidence time-of-flight mass spectrometry. Fragment ion energies exceeding several 10 eV are observed which have the potential to induce subsequent damage in a biological environment. Deoxyribose molecules from the DNA backbone are found to be most sensitive to keV ion impact and thus represent the weakest link in the DNA structure. Comparative studies on isolated molecules and molecules embedded in clusters reveal that intermolecular hydrogen bonds strongly affect the fragmentation dynamics of the DNA building blocks under study.

MO 16.5 Di 14:00 Poster C1

IR Spectroscopy of self-associated adenine derivates — •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

Self-association of 9-substituted adenine derivatives were investigated via IR-spectroscopy in $CDCl_3$ solutions. The infrared spectra of 9-ethyladenine and N-methyl-9-ethyladenine and its aggregates are presented in the mid and near IR spectral regions. Wavelength dependent absolute extinction coefficients of the monomer and dimers are presented on the basis of a simple deconvolution method which is explained in detail. 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 16.6 Di 14:00 Poster C1

The Influence of Seasonal Changes of the Day-Night Rhythm on the Composition of Hamster Bones Investigated by Raman Spectroscopy — •Jing Shen[1,2], Jiming Hu[2], Alexander Lerchl[1], and Arnulf Materny[1] — [1]Jacobs University Bremen, Germany — [2]Wuhan University, China

Raman spectroscopy is a non-destructive method, which can provide vibrational information on molecular level for biomedical samples. The change of the light and dark phases (photoperiods) considerably influences the vital functions of Djungarian hamsters. For example, it has been proven that a winter-time photoperiod results in a decline of body weight and is associated with changes of the gonadal function and fur color [1]. In our study, Raman spectroscopy is applied to observe bone compositional differences between long- (16L:8D) and short-day (8L:16D) photoperiod Djungarian hamsters. The bones were cut perpendicularly to the diaphysis at the condyle and in the middle of the diaphysis in order to have access to both cortical bone and trabeculae.

Spectra were obtained from different points of each sample and were then averaged. Our results demonstrate that long-day cortical bone samples have a higher phosphate-to-carbonate ratio in both femur and tibia.

[1] A. Lerchl *et al.*, *Neuroendocrinology* **57**,359 (1993).

MO 16.7 Di 14:00 Poster C1

Time-Resolved Spectroscopy on Molybdo Iron-Sulfur Flavoproteins — •Florian Spreitler[1], Astrid Pelzmann[2], Ortwin Meyer[2], and Jürgen Köhler[1] — [1]Experimentalphysik IV and BIMF, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany — [2]Mikrobiologie, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany

Flavoproteins are of great importance in nature because they function in several life-sustaining processes, such as cellular respiration, redox biochemistry, purine metabolism and the oxidation of CO. Their common cofactor flavin adenine dinocleotide (FAD), which can be bound in a covalent or non-covalent fashion, is thought to be fine-tuned by the respective protein matrix both in its redox properties and the exposure of certain atoms to the solvent.

Our main objective is to study the fast photophysics of FAD in different enzymes and enzyme mutants on timescales between 1 ps and 10 ns using a versatile streak camera setup. The work will also resolve structure-function relationships of the FAD binding site during catalysis and at different states of reduction.

Here, we present time-resolved fluorescence spectra of the FAD cofactor in three structurally similar molybdo iron-sulfur flavoproteins, which are the [$CuSMoO_2$] CO dehydrogenase from *Oligotropha carboxidovorans*, the [$MoSO_2$] xanthine dehydrogenase from chicken liver and the [$MoSO_2$] xanthine oxidase from bovine milk.

MO 16.8 Di 14:00 Poster C1

Mid and Near-Infrared spectra of conformers of H-Pro-Trp-OH and H-Trp-Ser-OH — Kai Seefeld[1], •Thomas Häber[1], Gernot Engler[1], Stefan Grimme[2], and Karl Kleinermanns[1] — [1]Institut für Physikalische Chemie, Heinrich-Heine Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany — [2]Theoretische Organische Chemie, Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, 48149 Münster, Germany

We present near and mid infrared-UV double resonance spectra of the natural di-peptides Pro-Trp and Trp-Ser. In the case of Pro-Trp two conformers are present in the supersonic expansion: a stretched conformer with fully extended backbone and a folded conformer with an $OH\cdots OC_{pep}$ hydrogen bond. Both conformers are stabilized by dispersion interaction between indole ring and peptide backbone and a $NH_{pep}/N_{proline}$ contact. Trp-Ser has two detectable conformers in supersonic expansions. The two conformers both have folded structures where both OH groups are involved in hydrogen bonds. The vibrational and conformational assignment is supported by DFT and *ab initio* calculations. An adequate description of the energetic order of different conformers requires the explicit inclusion of dispersion. The lowest energy conformers in both systems have peptide backbones that lie on top of the indole ring.

MO 16.9 Di 14:00 Poster C1

Radiation damage studies on water-embedded biomolecules — •Sadia Bari[1], Maarten Inklaar[1], Dominik Gosset[2], Femke van Seijen[1], Ronnie Hoekstra[1], and Thomas Schlathölter[1] — [1]KVI Atomic Physics, University of Groningen, The Netherlands — [2]ENSIAME, Valenciennes, France

The current increasing social and corporate interest in proton- and heavy ion-therapy of malignant tumors now results in the construction of first particle treatment centers. The chemical and biological aspects of biological radiation damage have been studied in great detail. However, little is known about biological radiation action on the molecular level and fs-timescales. First studies focused on gas phase DNA related molecules and neglected influences of the chemical environment.

To investigate these influences we built an electrospray ionization (ESI) source to form clusters from DNA molecules surrounded by water. Cooling and mass selection in a RF quadrupole ion trap ensures sufficient cluster density. After keV-ion irradiation collision products are extracted from the trap into a time-of-flight mass spectrometer.

MO 16.10 Di 14:00 Poster C1

The Interplay between Symmetry and Electronic Structure of Pigment-Protein Complexes from Purple Bacteria — •Ralf Kunz[1], Martin Richter[1], Silke Oellerich[1], Jürgen Baier[1], Thomas Prem[1], Francesco Francia[2], Giovanni Venturoli[2], Dieter Oesterhelt[3], June Southall[4], Richard Cogdell[4] und Jürgen Köhler[1] — [1]Experimentalphysik IV, Universität Bayreuth — [2]University of Bologna — [3]MPI für Biochemie, Martinsried — [4]University of Glasgow

A recent rather low resolution X-ray crystal structure of the RC-LH1 core complex from the photosynthetic purple bacterium *Rps. palustris* showed the presence of a physical gap in the LH1 ring. The presence of such a gap, though functionally critical for the cyclic electron transport in the photosynthetic process, has become very controversial. We have now applied single-molecule spectroscopy to the RC-LH1 complexes of the purple bacteria *Rps. palustris* and *Rb. sphaeroides (pufX- strain)* to demonstrate that there is such a gap in the LH1 ring structure. More than 80% of the complexes from *Rb. sphaeroides* only show broad absorption bands, whereas all of the measurable complexes from *Rps. palustris* also have a narrow line at the low-energy end of their spectrum. We describe how the presence of this narrow feature indicates the presence of a gap in the electronic structure of the LH1 from *Rps. palustris*, which provides strong support for the physical gap that was previously modelled in its X-ray crystal structure.

MO 16.11 Di 14:00 Poster C1

Fluorescence correlation spectroscopy on flavoproteins — •Christian Brock[1], Florian Spreitler[2], Astrid Pelzmann[3], Ortwin Meyer[4], and Jürgen Köhler[5] — [1]Lehrstuhl für Experimentalphysik 4, Universität Bayreuth — [2]Lehrstuhl für Experimentalphysik 4, Universität Bayreuth — [3]Lehrstuhl für Mikrobiologie, Universität Bayreuth — [4]Lehrstuhl für Mikrobiologie, Universität Bayreuth — [5]Lehrstuhl für Experimentalphysik 4, Universität Bayreuth

We use fluorescence correlation spectroscopy to investigate the binding properties of CO-dehydrogenase, a flavoenzyme that plays an important role in the respiratory chain of the CO-oxidizing bacterium Oligotropha carboxidovorans. CO-dehydrogenase is labeled with fluorescein, and the change of its diffusion-coefficient upon binding to a lipid vesicle is monitored. This experiment will be repeated with modified versions of the enzyme, lacking certain functional groups that are supposed to be responsible for binding. Furthermore, triplet kinetics of FAD and riboflavin have been analyzed.