BP 29: Biomolecular Spectroscopy

Time: Thursday 14:30–17:00 Location: H45

BP 29.1 Thu 14:30 H45

Determining the structure of Ac-Ala$_n$LysH$^+$ *in vacuo*: computational spectroscopy using DFT — •Mariana Rossi, Volker Blum, Peter Kupser, Gert von Helden, Frauke Bierau, Gerard Meijer, and Matthias Scheffler — Fritz-Haber-Institut, D-14195 Berlin, Germany

Well defined secondary structure motifs (e.g., helices) in polypeptides can be systematically studied in vacuo, offering a unique "clean room" condition to quantify the stabilizing intramolecular interactions. Here we address theoretically the structure of alanine polypeptides Ac-Ala$_n$LysH$^+$ (n=5,10,15), for which gas-phase helical structure was indicated in experiment [1]. Using van der Waals (vdW) corrected [2] Density Functional Theory (DFT), we present vibrational spectra and compare to room temperature multiple photon IR spectroscopy data obtained at the FELIX free electron laser. For the longer molecules (n=10,15) α-helical models provide good qualitative agreement (theory vs. experiment) already in the harmonic approximation. For Ac-Ala$_5$LysH$^+$, the predicted lowest energy conformer ("g-1") in vdW corrected DFT (PBE, B3LYP, revPBE) is not a simple helix. However, the harmonic free energy suggests that g-1 and the lowest-energy α-helical conformers are energetically close at 300 K, and thus might all coexist in experiment. Consistently, their calculated vibrational spectra agree with experiment, but only if anharmonic effects are included by explicit molecular dynam- ics simulations. [1] R. Hudgins *et al.*, JACS **120**, 12974 (1998) [2] A. Tkatchenko and M. Scheffler, PRL **102**, 073005 (2009)

BP 29.2 Thu 14:45 H45

Multivariate analysis for surface-enhanced Raman scattering (SERS) probe multiplexing and imaging in biological matrices — •Andrea Matschulat[1,2], Daniela Drescher[1,2], and Janina Kneipp[1,2] — [1]Institut für Chemie, HU, Brook-Taylor-Str. 2, 12489 Berlin — [2]Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstätter-Str.11, 12489 Berlin

Raman Spectroscopy as a non-destructive spectroscopic technique allows the study of vibrational fingerprints by which chemical and biological compounds can be identified. An improvement of the spatial resolution on the nm-scale is provided by local optical fields surrounding plasmonic nanostructures which are excited by the incident electromagnetic field. Such so-called surface-enhancement provides more sensitive detection. SERS has therefore attracted considerable interest for its application in bioanalytical chemistry. SERS offers numerous opportunities in the study of spectral changes during molecular interactions in complex biosystems. We demonstrate a multivariate approach for SERS hybrid probe multiplexing and imaging implementing principal component analysis and cluster algorithms. As a first application, we introduced two biocompatible Raman reporter molecules attached to Au nanoaggregates into living 3T3-cells. Such a hybrid probe approach enables the identification of different SERS probes in multiplexed experiments. We present results of hyperspectral mapping analysis providing us information about the cellular uptake, localization and amount of both reporter molecules inside the biosystem.

BP 29.3 Thu 15:00 H45

Characterization of artificial peptide receptors by UV resonance Raman spectroscopy and non-negative matrix factorization — •Christoph Herrmann[1], Stephan Niebling[1], Sunil Kumar Srivastava[1], Carsten Schmuck[2], and Sebastian Schlücker[1] — [1]Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49069 Osnabrück — [2]Institut für Organische Chemie, Universität Duisburg-Essen, Universitätsstr. 5, 45141 Essen

Guanidiniocarbonyl pyrroles are artificial peptide receptors which serve as model systems for investigating the principles of peptide binding. Their carboxylate binding site (CBS) can be selectively monitored by UV resonance Raman (UVRR) spectroscopy. UVRR spectra of guanidiniocarbonyl pyrroles we recorded at different pH values in the range of 4 to 9 in order to characterize the corresponding acid/base equilibrium. By using non-negative matrix factorization (NMF), we were able to extract the pure spectra of the neutral and protonated CBS species from the experimental UVRR spectra. This allowed the quantification of their relative contributions and the site specific pKa determination of the CBS in these artificial peptide receptors.

BP 29.4 Thu 15:15 H45

Conformation studies of the gram-negative-bacteria protein TonB by pulse EPR — •Silvia Domingo Köhler[1], Annemarie Weber[2], Wolfram Welte[2], and Malte Drescher[1] — [1]Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany — [2]Department of Biology, University of Konstanz, 78457 Konstanz, Germany

To transport Iron complexed in ferric siderophores through the outer membrane of gram-negative bacteria energy is required. It is proposed that a complex composed in particular by the TonB protein and anchored in the inner membrane opens channels in the outer membrane. The energy needed is only available in the inner membrane, in form of the proton motive force. Structure and dynamics of the protein TonB plays a key role in unraveling how the energy is transferred to the outer membrane, in order to induce a conformational change in the outer membrane receptors. However, the structure of TonB is not completely determined and the mechanism of energy transduction remains still unclear.

To unravel structure and functionality of TonB site-directed spin-labeling in combination with pulsed electron paramagnetic resonance (EPR) techniques is an outstandingly suitable tool. Determining conformation and conformational changes of TonB helps to elucidate a mechanism which has general implications for signal transduction within and between proteins.

BP 29.5 Thu 15:30 H45

Motional effects on coherent exciton transport in a chain — •Markus Tiersch[1,2], Ali Asadian[1,2], Gian Giacomo Guerreschi[1,2], Jianming Cai[1,2], Sandu Popescu[3], and Hans Briegel[1,2] — [1]Institut für Quantenoptik und Quanteninformation der Österreichischen Akademie der Wissenschaften, Innsbruck, Austria — [2]Institut für Theoretische Physik, Universität Innsbruck, Technikerstraße 25, A-6020 Innsbruck, Austria — [3]H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, United Kingdom

In a reduced model of coherent excitation transport in α-helical polypeptides, individual amide units in a chain carry the excitation, and are coupled through dipol-dipol interactions. Vibrations of the chain cause a modulation of the distance dependent dipolar coupling between the individual sites, and thereby influence the transport efficiency through the chain. In this setting, we report on the motion-induced, effective locking and guiding of excitations, and investigate control mechanisms to enhance the transport through the chain.

15 min. break

BP 29.6 Thu 16:00 H45

Pigment fluorescence in protein environment — •Franz-Josef Schmitt[1], Heinrich Südmeyer[2], Kai Reineke[1], Insa Kahlen[1], Joachim Börner[1], Max Schoengen[1], Patrick Hätti[1], Hans Joachim Eichler[1], and Hans-Joachim Cappius[2] — [1]Berlin Institute of Technology, Berlin — [2]Laser- und Medizintechnologie GmbH, Berlin

The electronic properties of organic molecules strongly depend on the local environment. Therefore it is difficult to detect specific molecules if the environment of the molecules is not clearly defined. On the other hand the fine tunig of the local protein environment leads to specific pathways for excitation energy migration between pigments in e.g. photosynthetic plant complexes and the influence of the environment is essential for the light harvesting functionality. In this study we compare the time resolved fluorescence of pigments (e.g. fluorescein, chlorophyll) and pigment protein complexes (e.g. Bovine serum albumin, water soluble chlorophyll binding protein and photosynthetic light harvesting complexes). The protein matrix has an own characteristic influence onto the chromophores and strongly diminishes the environmental influence onto the chromophores. The fluorescence of fluoresceine and chlorophylle molecules on glass surface is strongly quenched while the pigments bound to protein complexes show only slight changes of the fluorescence dynamics due to the surface contact.

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BP 29.7 Thu 16:15 H45

Excitation energy transfer in the Phycobiliprotein Antenna of the cyanobacterium Acaryochloris marina investigated by transient fs absorption spectroscopy. — •Collins Nganou[1], Moritz Grehn[1], Christoph Theiss[1], Marco Vitali[2], Franz-Joseph Schmitt[1], Hans Joachim Eichler[1], and Hann-Jörg Eckert[2] — [1]Institute of Optics, Technical University Berlin, Straße des 17. Juni 135, Berlin-Germany — [2]Max-Volmer-Laboratory for Biophysical Chemistry, Technical University Berlin, Straße des 17. Juni 135, Berlin-Germany

The investigation of excitation energy transfer (EET) in the antenna system of Acaryochloris marina containing both chlorophyll (Chl) d and phycobiliprotein (PBP) as light harvesting pigments continue to be a case of debate in the scientific community. The PBP-antenna is a rod-shaped antenna of three homo-hexamers containing phycocyanin (PC) and one hetero-hexamer of PC and allophycocyanine (APC). In the present work we discuss the EET in isolated PBP-antennae by transient fs absorption spectroscopy measurements and show that the presence of phosphate in the buffering medium is an important requirement to preserve the EET between the PBP pigments.

BP 29.8 Thu 16:30 H45

Describing transient Fluorescence induction curves by modelling the electron transfer of photosystem II — •Joachim Börner[1], Franz-Josef Schmitt[1], Hans Joachim Eichler[1], Athina Zouni[2], and Gernot Renger[2] — [1]Institute of Optics and Atomic Physics, Berlin Institute of Technology, Germany — [2]Max-Volmer-Laboratory for biophysical chemistry, Berlin Institute of Technology, Germany

In this work a generalised PS II model for the simulation of fluorescence induction curves is presented. Fluorescence induction curves were measured with continuous laser illumination on isolated core complexes from the thermophilic cyanobacterium Thermosynechococcus elongatus and hole cells of the green algae Chlorella pyrenodoisa chick. Perfect data fit was achieved within the framework of a model for the PS II reaction pattern comprising electron transfer reactions to the exogenous electron acceptor $K_3Fe(CN)_6$ in core complexes and to the endogenous plastoquinone in chlorella cells. Based on data reported in the literature a consistent set of rate constants was obtained for electron transfer at the donor and acceptor side of PS II. The simulations based on the model of the PS II reaction pattern provide information on the time courses of population probabilities of different PSII states in photosynthetic samples under various conditions (e.g. presence of herbicides, other stress conditions, excitation with actinic pulses of different intensity and duration).

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BP 29.9 Thu 16:45 H45

Photocycle Dynamics of the E149A Mutant of Cryptochrome 3 from *Arabidopsis thaliana* — Peyman Zirak[1], •Alfons Penzkofer[1], Judit Moldt[2], Richard Pokorny[2], Alfred Batschauer[2], and Lars-Oliver Essen[3] — [1]Institut II - Experimentelle und Angewandte Physik, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg — [2]Fachbereich Biologie, Pflanzenphysiologie/Photobiologie, Philipps-Universität, Karl-von-Frisch-Str. 8, 35032 Marburg — [3]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str., 35032 Marburg

The E149A mutant of the cryDASH member cryptochrome 3 (cry3) from *Arabidopsis thaliana* was characterized *in vitro* by absorption and emission spectroscopy. The mutant protein non-covalently binds the cofactor flavin adenine dinucleotide (FAD), but not the second cofactor 5,10-methenyl-tetrahydrofolate (MTHF). Thus, the photodynamics caused by FAD is accessible without the intervening coupling with MTHF. In dark adapted cry3-E149A, FAD is present in the oxidized form (FAD_{ox}), semiquinone form ($FADH^{\cdot}$), and anionic hydroquinone form ($FAD_{red}H^-$). Blue-light photo-excitation of previously unexposed cry3-E149A transfers FAD_{ox} to the anionic semiquinone form ($FAD^{\cdot -}$) with a quantum efficiency of 0.02 and a back recovery time of 10 s (photocycle I). Prolonged photo-excitation leads to an irreversible protein re-conformation leading to a change in the photocycle dynamics with photo-conversion of FAD_{ox} to $FADH^{\cdot}$ (efficiency 0.00032), of $FADH^{\cdot}$ to $FAD_{red}H^-$ (efficiency 0.016), and thermal back equilibration in the dark on a minute timescale (photocycle II).