

CPP 37: Biopolymers (joint session CPP/BP)

Time: Thursday 14:30–17:30

Location: ZEU 114

CPP 37.1 Thu 14:30 ZEU 114

Secondary structure of polyaniline peptides [Ac-Ala_nLysH⁺ (n=5, 10, 15, 19)] in vacuo – part I (experiment) — ●PETER KUPSER, FRAUKE BIERAU, GERT VON HELDEN, MARIANA ROSSI, VOLKER BLUM, MATTHIAS SCHEFFLER, and GERARD MEIJER — Fritz-Haber-Institut, D-14195 Berlin, Germany

While vibrational spectroscopy is one of the key techniques to determine the three-dimensional folding arrangements of biological molecules in solution, infrared experiments of gas-phase peptides and proteins can provide information on intrinsic molecular structural properties without interactions with the surrounding solvent molecules [1]. This is also of great interest for theoreticians to test and enhance their models for determining the structure of biomolecules.

Ac-Ala_n-LysH⁺ (n=5, 10, 15, 19) peptides in the gas phase can serve as model systems for a helical secondary structure [2]. Infrared multiphoton dissociation experiments in the regions of the amide I (C=O stretching vibration around 1700 cm⁻¹) and amide II (N-H bending vibration around 1500 cm⁻¹) band on these polyaniline peptides at room temperature were performed using the free electron laser FELIX. The position of the amide I band shifts to lower energies with increasing number of alanines in the chain. Experimental results will be presented and discussed. [1] G. von Helden *et al.*, PCCP 7, 1345 (2005). [2] R. R. Hudgins *et al.*, JACS 120, 12974 (1998).

CPP 37.2 Thu 14:45 ZEU 114

Secondary structure of polyaniline peptides [Ac-Ala_nLysH⁺ (n=5, 10, 15)] in vacuo – part II (density functional theory) — ●MARIANA ROSSI, VOLKER BLUM, PETER KUPSER, GERT VON HELDEN, FRAUKE BIERAU, GERARD MEIJER, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut, D-14195 Berlin, Germany

Predicting the conformation(s) of biomolecules from first principles is an important challenge, requiring *both* an accurate energetic description of single conformers *and* an efficient strategy to explore the combinatorial explosion of potential candidate structures. We here study the secondary structure of Ac-Ala_nLysH⁺ (n=5, 10, 15) polyaniline peptides *in vacuo*, based on density-functional theory in the generalized gradient approximation with van der Waals corrections (GGA+vdW), using the FHI-aims code [1]. We verify our results by comparing calculated vibrational spectra with experimental room-temperature multiphoton IR spectra obtained using the FELIX free-electron laser. We use a force field (OPLS) to screen roughly the conformational energetics of as many structure candidates as possible (>10⁴ in practice), following up with GGA+vdW for a wide range of low-energy conformers. Consistent with earlier indications [2], we find that Ac-Ala₅LysH⁺ is helical, with a close energetic competition between α - and 3_{10} -like conformers. We show how the LysH⁺ termination acts to induce helices also for longer peptides, and that the inclusion of vdW contributions is critical to decide the detailed energy hierarchy. [1] V. Blum, *et al.*, Comput. Phys. Comm., accepted (2008). [2] R. Hudgins *et al.*, JACS 120, 12974 (1998).

CPP 37.3 Thu 15:00 ZEU 114

Role of van der Waals interactions for the intrinsic stability of polyaniline helices — ●ALEXANDRE TKATCHENKO¹, VOLKER BLUM¹, JOEL IRETA², and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Dep. Quimica, UAM-Iztapalapa, Mexico

The helical motif is an ubiquitous conformation adopted by amino acid residues in a protein structure and helix formation is the simplest example of the protein folding process. How stable is the folded peptide helix in comparison to a random coil structure? What are the interactions responsible for stabilizing the helical conformation? Answering these questions has thus a direct implication for understanding protein folding. In this work we use density functional theory (DFT) augmented with a non-empirical correction for van der Waals (vdW) forces to study the stability of alanine polypeptide helices *in vacuo*. We find a large stabilization of the native helical forms when vdW correction is used. It amounts to 121%, 157% and 83% on top of the Perdew-Burke-Ernzerhof (PBE) functional in the case of infinite α , π and 3_{10} helices, respectively. Thus, the experimentally observed α helix is significantly stabilized by vdW forces both over the fully extended and the 3_{10} conformations. Our findings also suggest an ex-

planation to the remarkable stability of gas-phase alanine helices up to high temperatures [M. Kohtani *et al.* JACS 126, 7420 (2004)].

CPP 37.4 Thu 15:15 ZEU 114

Investigation of pulp fiber surfaces and cross-sections using atomic force microscopy — ●FRANZ SCHMIED^{1,4}, CHRISTIAN TEICHERT^{1,4}, LISBETH KAPPEL^{2,4}, ULRICH HIRN^{2,4}, and ROBERT SCHENNACH^{3,4} — ¹Institute of Physics, Montanuniversität Leoben, Franz Josef Straße 18, 8700 Leoben, Austria — ²Institute of Solid State Physics, Graz University of Technology, Petersgasse 16/2, 8010 Graz — ³Institute for Paper, Pulp and Fiber Technology, Graz University of Technology, Kopernikusgasse 24/II, 8010 Graz — ⁴CD-Laboratory for Surface Chemical and Physical Fundamentals of Paper Strength, Graz University of Technology, Petersgasse 16/2, 8010 Graz

Paper is made up of wood fibers. The nano- and microstructure of the fibers, as well as the influence of this structure on the inter-fiber bond strength are not yet completely understood. For improvement of paper strength, a deeper insight into this correlation is desirable because the structure is - besides the chemical composition - the most important influence on the mechanical paper properties. For our investigations we applied atomic-force microscopy (AFM) with phase imaging to study the surface of unbleached chemical pulp fibers and visualized the single fibrils. Further we report investigations of treated pulp fiber surfaces with different amounts of lignin. We quantify the geometry of precipitated lignin and characterize cross-sections of embedded paper sheets. The study showed that AFM is an appropriate tool to characterize the surface morphology of chemical pulp fibers on the nanometer scale.

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Silkworm silk under tensile stress as a function of humidity investigated by neutron spectroscopy — ●WIEBKE KNOLL¹, TILO SEYDEL², MALTE OGURRECK¹, IMKE DIDDENS³, CEDRIC DICKO³, and MARTIN MÜLLER⁴ — ¹IEAP, Universität Kiel — ²ILL, Grenoble — ³Department of Zoology, Oxford — ⁴GKSS, Geesthacht

Natural silk fibres exhibit extraordinary mechanical properties, combining high tensile strength with a high elongation at failure. The mesoscopic structure with crystalline regions embedded in a softer disordered matrix is the key to these properties. We measured the molecular vibrational response of Bombyx mori silkworm silk fibres *in situ* upon externally applied tensile stress using cold neutron time-of-flight spectroscopy. Adding to a previous study on dry silk fibers we recently investigated humid silk fibers. The aligned silk fibers are therefore exposed to a tensile force along the fiber axis generated by a stretching machine in a humidity chamber. The applied force was sufficient to reach the yield point of plastic deformation. It is already known from X-ray studies that most of the deformation upon extension of the fibres is due to the amorphous regions of the silk. The neutron results on dry fibers indicate that the externally applied force is not reflected by any noticeable effect on the molecular vibrational or diffusional/reorientational properties of the amorphous silk protein. However, on humid fibers we observed a quasielastic broadening of the scattering function, which is due to polymer chain mobility enhanced by the adsorbed water. This effect increases with stretching the humid silk fibers.

CPP 37.6 Thu 15:45 ZEU 114

Anisotropic elastic properties of cellulose measured using inelastic X-ray scattering — IMKE DIDDENS¹, BRIDGET MURPHY¹, MICHAEL KRISCH², and ●MARTIN MÜLLER³ — ¹IEAP, Universität Kiel, 24098 Kiel — ²ESRF, BP 220, 38043 Grenoble, France — ³GKSS Forschungszentrum Geesthacht, Max-Planck-Str. 1, 21502 Geesthacht

Plant fibers such as linen are remarkably stiff materials in the longitudinal direction of the fiber. As plant cell walls are composites made of cellulose nanocrystals, the so-called microfibrils, embedded in a disordered matrix, those nanocrystals should exhibit an even higher elastic modulus *G*. We have determined the elastic properties of cellulose microfibrils via the sound velocities measured by inelastic X-ray scattering (IXS). The IXS technique is particularly sensitive to crystal properties by discriminating the contribution of disordered material. A strong anisotropy is observed [1], with a much lower elastic modulus

perpendicular to the fiber direction ($G1 = 15$ GPa) than parallel to it ($G2 = 220$ GPa). The latter modulus is considerably higher than all values previously determined and will have a significant impact on models for the elastic properties of cellulose microfibrils and of composites based on them.

[1] I. Diddens, B. Murphy, M. Krisch, M. Müller, *Macromolecules*, ASAP online, in press.

15 min. break

CPP 37.7 Thu 16:15 ZEU 114

Proteins on Surfaces investigated by Microbeam Grazing Incidence Small Angle X-ray Scattering — ●RONALD GEBHARDT¹, CHRISTIAN RIEKEL¹, CHARLOTTE VENDRELY², MANFRED BURGHAMMER¹, and PETER MÜLLER-BUSCHBAUM³ — ¹European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France — ²Université de Cergy-Pontoise, ERMECE, F-95000, Cergy-Pontoise, France — ³TU München, Physik Department E13, München, Germany

Grazing incidence small angle scattering with a 1 micron x-ray beam (μ GISAXS) is applied to study structural ordering of casein micelles and fibroin in solution cast films. μ GISAXS scans provide the possibility to locate highly ordered areas and to investigate variation in the molecular packing.

In the case of the casein micelles, ordered film structures have been generated by decreasing their natural size dispersion. While dynamic light scattering was used to characterize the different size fractions in solution, μ GISAXS and roughness are measured on the resulting casein films. GISAXS-Patterns are analyzed by simulations providing the dimension and nearest neighbor distances of casein micelles.

In the case of fibroin, ordering of nano-fibers formed during the drying process is investigated. The experimental data are analyzed by simulations and compared to SEM, AFM and Raman scattering experiments.

CPP 37.8 Thu 16:30 ZEU 114

Adsorption kinetics of proteins on tailored surfaces: An ellipsometry study — ●SAMUEL GRANDTHYLL, HENDRIK HÄHL, HUBERT MANTZ, and KARIN JACOBS — Saarland University, Experimental Physics, D-66041 Saarbruecken, Germany

The adsorption of proteins onto solid surfaces is an everyday phenomenon. For a better understanding of the driving forces inducing the formation of the initial protein layer, we have studied the adsorption kinetics of three different proteins: Bovine serum albumin (BSA), α -amylase and lysozyme.

Our focus had been on the influence of the substrate, where lock-and-key mechanism between protein and surface were absent. It is already textbook knowledge that protein adsorption is influenced by short-range forces arising from the surface chemistry and Coulomb interaction due to unscreened charges. We could show that also long-range van der Waals forces present between the protein and the sample substrate are important. These interactions depend on the thickness of the oxide layer of a silicon wafer and thus are easily alterable [1].

Ellipsometry measurements show that the kinetics of BSA and α -amylase on native thin oxide layers does not follow a standard adsorption model, because the kinetics curve is separated by two kinks. By including conformational changes of the proteins into Monte Carlo simulations, the experimental results could be qualitatively reproduced [2].

[1] A. Quinn et al., *EPL*, **81**, 56003, (2008)

[2] M. Bellion et al., *J. Phys.: Condens. Mat.* **20**, 404226, (2008)

CPP 37.9 Thu 16:45 ZEU 114

Translocation of biopolymers through narrow and wide nanopores: a multiscale computational approach — ●MARIA FYTA^{1,5}, SIMONE MELCHIONNA^{1,2}, MASSIMO BERNASCHI³, SAURO SUCCI^{3,4}, and EFTHIMIOS KAXIRAS^{1,4} — ¹Department of Physics and School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA — ²INFN-SOFT, Department of Physics, Università di Roma La Sapienza, P.le A. Moro 2, 00185 Rome, Italy — ³Istituto Applicazioni Calcolo, CNR, Viale del Policlinico 137, 00161,

Roma, Italy — ⁴Initiative in Innovative Computing, Harvard University, Cambridge, MA, USA — ⁵Present address: Physics Department, Technical University of Munich, Germany

Our recently developed novel multiscale approach which concurrently couples a mesoscopic fluid solvent with molecular motion has been efficiently applied to the problem of biopolymer translocation through nanopores. We present results from thousands of numerical simulations of long biopolymers up to 8000 monomers passing through pores of various sizes. The statistical scaling behavior of the translocation process is reproduced with remarkable accuracy. Our results provide valuable insight into the cooperative aspects of biopolymer and hydrodynamic motion. The statistical and dynamical features of the translocation process are incorporated into a phenomenological model for the power law dependence of the translocation time on the biopolymer length. In the case of wide pores, there is clear evidence of folding quantization, leading to a deviation from the single-exponent power-law characterizing the single-file translocation through narrow pores.

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Hydration behavior of casein micelles in thin film geometry: A GISANS study — ●EZZELDIN METWALLI¹, JEAN-FRANCOIS MOULIN², RONALD GEBHARDT³, ROBERT CUBITT⁴, ALEXANDER TOLKACH⁵, ULRICH KULOZIK⁵, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik Department LS E13, James-Frank-Str.1, 85747 Garching, Germany — ²FRM II, TU München, 85747 Garching, Germany — ³ESRF, b.p. 220, 38043 Grenoble, France — ⁴ILL, 6 rue Jules Horowitz, b.p. 156, 38042 Grenoble, France — ⁵TU München, Chair for Food Process Engineering and Dairy Technology, 85354 Freising-Weihnstefan, Germany

The water content of the casein micelle films in water vapor atmosphere is investigated using time-resolved grazing incidence small-angle neutron scattering (GISANS). Initial dry casein films are prepared with spin coating method. At 30 °C the formation of a water equilibrated casein protein film is reached after 11 min with a total content of 0.36 g water/ g protein. With increasing water vapor temperature up to 70 °C an increase in the water content is found. With GISANS, lateral structures in the nano-meter scale are resolved during the swelling experiment at different temperatures and modeled using two spheres named micelles and mini-micelles. Upon water uptake, molecular assemblies in the size range of 15 nm (mini-micelle) is attributed to the formation of high contrast D2O outer shell on the small objects that already exist in the protein film [1]. These results are discussed and compared with various proposed models on the casein micelle structures. [1] E. Metwalli et al., *Langmuir* accepted 2008.

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Photo-CIDNP study of transient radicals of Met-Gly and Gly-Met peptides — OLGA MOROZOVA¹, SERGEY KORCHAK², HANS-MARTIN VIETH², and ●ALEXANDRA YURKOVSKAYA^{1,2} — ¹International Tomography Center, Institutskaya 3a, Novosibirsk, Russia — ²FB Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

Photo-reactions of methionine containing dipeptides, glycylmethionine (Gly-Met) and methionylglycine (Met-Gly) were studied by time-resolved Chemically Induced Dynamic Nuclear Polarization (CIDNP) a method particularly sensitive to short-lived radical species. In aqueous solution we established several competing reaction pathways following triplet quenching of the photosensitizer 4-carboxybenzophenone depending on the pH: for Gly-Met electron transfer from the sulfur atom takes place, also from the terminal amino group. Two channels of triplet quenching are distinguishable also for Met-Gly: electron transfer from the amino group and from the sulfur atom, here with the formation of a cation radical with a three electron two center S-N bond. At $\text{pH} < \text{pKa}$ of the terminal amino group Met-Gly forms a linear S-centered radical succeeded by a five-membered cyclic radical. At $\text{pH} > \text{pKa}$ both peptides form aminium radicals by electron transfer from their N-terminal amino group with deprotonation to the aminyl radical. The radicals were characterized using the dependence of CIDNP on the magnetic field. The potential of the CIDNP techniques in studying other complex biological radical reactions will be discussed. Financial support by the RFBR projects # 08-03-00539, EU FP6 projects "Bio-DNP" and MIF2-CT-2006-022008 is acknowledged.