

CPP 6: Dynamics of Molecular Systems

Time: Monday 14:30–15:45

Location: H47

CPP 6.1 Mon 14:30 H47

Confinement effects on the molecular dynamics of thin polymer films — ●ANATOLI SERGHEI and FRIEDRICH KREMER — Universität Leipzig, Institut für experimentelle Physik I, Linnestr. 5, 04103 Leipzig

The molecular dynamics in thin films of polymers having different (linear, hyperbranched and dendritic) macromolecular architectures is discussed. Based on measurements by means of Broadband Dielectric Spectroscopy, capacitive scanning dilatometry and AC-calorimetry, the following issues are addressed: (i) What is the molecular mechanism of the confinement-effects? (ii) What role plays the macromolecular architecture in the dynamics of confined polymers? (iii) Do different experimental techniques deliver similar results when applied to investigate the dynamics of confined polymers? (iv) Does the presence of a free interface lead to shifts in the dynamics glass transition of thin polymer films? In order to address the last question, a novel experimental approach is demonstrated, which enables one to measure the molecular dynamics in ultra-thin organic layers having one free interface. [1] A. Serghei, F. Kremer, Phys. Rev. Lett. 91, 165702 (2003). [2] A. Serghei et al., Phys. Rev. E 71, 061801 (2005). [3] A. Serghei et al., Eur. Phys. J. E 17, 199 (2005). [4] A. Serghei et al., J. Polym. Sci. B 44, 3006 (2006). [5] A. Serghei, M. Tress, and F. Kremer, Macromolecules, in press (2006). [6] A. Serghei, and F. Kremer, Rev. Sci. Instrum. 77, 116108 (2006).

CPP 6.2 Mon 14:45 H47

Low-temperature spectral dynamics of single TDI molecules in alkane matrixes — ●SEBASTIAN MACKOWSKI, STEPHAN WÖRMKE, MORITZ EHRL, and CHRISTOPH BRÄUCHLE — Department of Chemistry and Biochemistry and Center for Nanoscience, Ludwig-Maximilians-University, D-81377 Munich, Germany

We use vibronic excitation approach to study the low-temperature (1.6K) fluorescence dynamics of the single TDI molecules in alkane matrixes. Four hosts were used, characterized with different length and parity: heptane, hexane, pentadecane and hexadecane. For every matrix, fluorescence trajectories of several tens of single molecules were measured. In the case of long-chain alkanes (pentadecane and hexadecane), the fluorescence of single TDI molecules has been found to be stable, showing only occasional spectral jumps of moderate energy ($<10\text{cm}^{-1}$). An average time between the jumps is 10 seconds and the jumps occur between well resolved levels. We have not observed any difference between the two matrixes. On the other hand, the spectral dynamics of TDI molecules embedded within the short-length alkane matrixes (heptane and hexane) is dramatically different. In these cases the spectral jumps are much more frequent, with average time between the two jumps being less than 1 second. In addition, we also observe significant, threefold increase in average energy of the jump. No qualitative differences between the two matrixes with short chain length were observed. The results suggest that matrixes composed of short chain molecules are more susceptible for translations and/or rotations which influence the spectral properties of single chromophores.

CPP 6.3 Mon 15:00 H47

The electronic structure and the hydrogen bond network of H₂O and D₂O studied by X-ray emission (XES) and X-ray absorption spectroscopy (XAS) in the soft X-ray range — ●MONIKA BLUM¹, OLIVER FUCHS¹, MARKUS WEIGAND¹, FLORIAN MAIER¹, EBERHARD UMBACH¹, LOTHAR WEINHARDT², MARCUS BÄR², CLEMENS HESKE², MICHAEL ZHARNIKOV³, MICHAEL GRUNZE³, and JONATHAN DENLINGER⁴ — ¹Universität Würzburg, Experimentelle Physik II, 97074 Würzburg — ²Dept. of Chem., University of Nevada, Las Vegas — ³Angew. Physikal. Chemie, Uni Heidelberg — ⁴ALS, Berkeley

The investigation of liquids by means of soft x-ray techniques is a tech-

nically challenging task since it requires a third generation synchrotron source combined with a high efficiency grating spectrometer and a wet cell with an ultra-thin window separating the liquid from ultra-high vacuum. With our flow-through wet cell we have investigated the electronic structure of various liquids including H₂O, D₂O, NaOH and NaOD.

The molecular dynamics within the time scale of the core hole lifetime (a few femtoseconds) lead to isotope and temperature effects of the measured liquids in both, XES and XAS spectra. These effects can be analyzed by the comparison of the XES spectra of H₂O and D₂O. Two different species can thus be identified. The observed isotope, energy and temperature dependent effects can be explained by these species involving tunneling processes within the hydrogen bond network.

CPP 6.4 Mon 15:15 H47

Investigation of the electronic structure of NH₃ and ND₃ in aqueous solution using x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) — ●M. WEIGAND¹, O. FUCHS¹, M. BLUM¹, F. MAIER¹, E. UMBACH¹, L. WEINHARDT², M. BÄR², C. HESKE², M. ZHARNIKOV³, M. GRUNZE³, and J. DENLINGER⁴ — ¹Universität Würzburg, Experimentelle Physik II, 97074 Würzburg — ²Dept. of Chem., University of Nevada, Las Vegas — ³Ang. Phys. Chemie, Uni Heidelberg — ⁴ALS, Berkeley

Soft x-ray spectroscopy of aqueous solutions at the carbon-, nitrogen- and oxygen-edge is a promising technique to investigate the electronic structure of biological systems in natural environment. Precise measurements require the use of a flow-through liquid cell to ensure thermodynamic equilibrium and to reduce beam-induced damage effects. Hitherto used Si₃N₄-windows denied access to the N-edge and showed contaminations limiting the viability of spectroscopy of solutions at the C- and O-edge. Using new ultra-thin SiC-membranes, the N-edge energy window is now open to measurements.

NH₃ and ND₃ provide an excellent test system to study the influence of H-bonds in aqueous solution, providing complementary information compared to the O-edge of H₂O and D₂O, which is currently in the focus of extensive investigations. XAS showed pronounced differences to the gas phase as well as strong isotopic effects, mirroring the behaviour of the water O-edge. RIXS results demonstrate excellent membrane properties and provide evidence of spectator and shake-up processes in NH₃ solutions.

CPP 6.5 Mon 15:30 H47

²H-NMR-Untersuchungen an hochdichtem amorphem Eis — ●MARCO SCHEUERMANN¹, BURKHARD GEIL², KATRIN WINKEL³ and FRANZ FUJARA¹ — ¹Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, 64289 Darmstadt — ²Lehrstuhl für Experimentelle Physik III, Universität Dortmund, Otto-Hahn-Str. 4, 44221 Dortmund — ³Allgemeine, Anorganische & Theoretische Chemie Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Österreich

In dieser Arbeit¹ werden ²H-Spin-Gitter-Relaxationsmessungen in Abhängigkeit von der Temperatur an den amorphen Eisformen Low-Density Amorphous (LDA), High-Density Amorphous (HDA) und Very-High-Density Amorphous (VHDA) vorgestellt. Die T₁-Relaxationszeiten werden als Monitor-Parameter verwendet, um die Kinetik der Übergänge von HDA nach LDA und VHDA nach LDA bei ambientem Druck zu untersuchen. Die Übergangstemperaturen von 108 K (HDA/LDA) und 120 K (VHDA/LDA) stimmen mit den Ergebnissen aus Neutronen-Streu-Experimenten überein². Im Übergang von VHDA nach LDA wird ein Zwischenzustand identifiziert, dessen dynamische Eigenschaften denen des HDA gleichen. Dieser HDA-ähnliche Zustand tritt jedoch bei Temperaturen auf, die höher sind als die Stabilitätsgrenze von HDA.

¹M. Scheuermann et al, J. Chem. Phys. 124, 224503 (2006)²M. Koza et al, Phys. Rev. Lett. 94, 125506 (2005)