

MO 12 Ultrafast Structural Changes

Zeit: Montag 14:00–16:00

Raum: H12

Fachvortrag

MO 12.1 Mo 14:00 H12

Bewegte Bilder auf atomarer Längen- und Zeitskala: Femtosekunden Röntgenbeugung — ●MATIAS BARGHEER — Max-Born-Institut, Max-Born-Str. 2a, 12489 Berlin

Die Funktion vieler physikalischer Systeme von Molekülen über weiche Materie bis hin zu Festkörpern beinhaltet Veränderungen der Gleichgewichtsstruktur. Durch Röntgenbeugung lassen sich Strukturen auf atomarer Längenskala exakt vermessen. Die Zeitskala der mikroskopischen Veränderungen wird durch die relevanten Schwingungsmoden bestimmt und liegt im Bereich von Femtosekunden bis Pikosekunden. Neuartige Quellen ultrakurzer Röntgenpulse - laserbasiert oder an Elektronenbeschleunigern - erreichen Pulsdauern von ca. 100 fs. Diese ultrakurze Belichtungszeit erlaubt es, den Ablauf einer strukturellen Veränderung durch Schnappschüsse zu verschiedenen Zeiten nach einer ultrakurzen Anregung des Systems zu filmen. Man kann somit einen selektiv angeregten, kohärenten Teil der Gitterdynamik beobachten, selbst wenn diese kollektive Bewegung eine kleinere Amplitude als die thermischen Fluktuationen hat. Anhand von drei Beispielen (Halbleiter-Nanostrukturen, Ferroelektrika und Molekülkristalle) wird in diesem Vortrag gezeigt, welche Informationen man aus der Beobachtung der Dynamik in Echtzeit ziehen kann, und welche Perspektiven sich daraus für die Ultrakurzzeit-Molekülphysik ergeben.[1,2]

[1] M. Bargheer, N. Zhavoronkov, Y. Gritsai, J. C. Woo, D. S. Kim, M. Woerner, and T. Elsaesser, *Science* 306, 1771 (2004)

[2] M. Bargheer, N. Zhavoronkov, M. Woerner, T. Elsaesser, *Minireview in PhysChemPhys*, accepted (2006)

MO 12.2 Mo 14:30 H12

Transiente Absorptionsspektroskopie an organischen Molekülkristallen aus DIABN — ●CHRISTOPHER ROOT, PETER GILCH, MARKUS BRAUN und WOLFGANG ZINTH — Lehrstuhl für Biomolekulare Optik, Oettingenstrasse 67, Ludwig-Maximilians-Universität München, 80538 München

Die Molekülgruppe der Aminobenzonitrile kann nach Photoanregung einen intramolekularen Ladungstransfer durchführen. Diese Vorgänge können in den beiden Vertretern Dimethylaminobenzonitril (DMABN) und Diisopropylaminobenzonitril (DIABN) in Lösung mittels transientser Absorptionsspektroskopie sichtbar gemacht werden.

Im kristallinen Festkörper kommen zusätzlich beobachtbare Effekte hinzu. Diese führen zu Absorptionsänderungen, die über mehrere hundert Pikosekunden hinweg zerfallen. Durch geeignete Wahl der Anregungsbedingungen kann man deren Einfluss auf die messbaren Signale gezielt beeinflussen. Die gezeigten Ergebnisse dienen als Grundlage für zeitaufgelöste Röntgenbeugungsexperimente, bei denen unter gleichen experimentellen Voraussetzungen die Auswirkung des Ladungstransfers beobachtet werden kann.

MO 12.3 Mo 14:45 H12

Ultrafast X-ray diffraction study of the molecular crystal DIABN — ●CLEMENS VON KORFF SCHMISING¹, MAREIKE KIEL¹, MATIAS BARGHEER¹, MICHAEL WOERNER¹, THOMAS ELSAESSER¹, CHRISTOPHER ROOT², MARKUS BRAUN², and WOLFGANG ZINTH² — ¹Max-Born-Institut, Max-Born-Str. 2a, 12047 Berlin — ²Lehrstuhl für Biomolekulare Optik, Oettingenstrasse 67, Ludwig-Maximilians-Universität München, 80538 München

We present x-ray diffraction data taken on single crystals and powder samples of the molecular crystal diisopropylaminobenzonitrile (DIABN), recorded with a femtosecond x-ray plasma source providing a time-resolution of few 100 fs. DIABN represents a model system for photoinduced charge transfer, and the induced intra-molecular motion is subject of a long standing controversy. The molecules are excited with 400 nm pump pulses to the locally excited state (LE). We measure the intensity of several Bragg reflections as a function of the time-delay between the pump pulse and the x-ray probe pulse. The diffraction transients are modulated on a 10 ps timescale with a surprisingly large amplitude of several percent, although the excitation density is only 10^{-4} . This suggests an interpretation in terms of inter-molecular dynamics, which we attribute to solvation of the excited state dipole in the polar solvent of the crystal itself. On the basis of the experimental findings we discuss the perspectives for studying ultrafast molecular processes by femtosecond x-ray diffraction.

MO 12.4 Mo 15:00 H12

Determination of the excited state twisting angle of the chromophore of green fluorescent protein — ●OMAR F. MOHAMMED¹, ANWAR USMAN¹, JIAN DONG², KYRYL M. SOLNTSEV², ERIK T. J. NIBBERING¹, and LAREN M. TOLBERT² — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany — ²School of Chemistry and Biochemistry, Georgia Institute of Technology; Atlanta, GA, USA

Whereas in wild type green fluorescent protein (GFP), the photochemical dynamics of the chromophore consists of a Förster cycle with excited state proton transfer and a high quantum yield for fluorescent emission, the chromophore in solution, p-hydroxybenzylidene-imidazolidinone (HBDI) shows ultrafast internal conversion. We report [J. Am. Chem. Soc. 127, 11214 (2005)] on ultrafast polarization-sensitive infrared (IR) spectroscopy of the excited state structure of HBDI, from which we draw conclusions on the importance of twisting motions. Our focus is on the orientation of the transition moment of the IR-active carbonyl stretching vibration of HBDI relative to that of the electronic transition dipole moment, which indicates that the C=O vibration acts as a spectator mode for the relative orientation of the phenolate and imidazolidinone groups. We have determined the anisotropy of the C=O vibration of HBDI in the S0 and S1 states for three charged configurations (anionic, neutral and cationic form). We find that our estimated value for the C=O bond vector in the S1-state can only be explained by a single twist of 120 degrees or a hula twist of 150 degrees, much larger than the twisting angle of 90 degrees found in quantum chemical calculations.

MO 12.5 Mo 15:15 H12

Structural Evolution in the Primary Stages of Trans/Cis Isomerization of the Chromophore in Photoactive Yellow Protein — ●KARSTEN HEYNE^{1,2}, OMAR F. MOHAMMED¹, ANWAR USMAN¹, JENS DREYER¹, ERIK T. J. NIBBERING¹, and MICHAEL A. CUSANOVICH³ — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born Strasse 2A, 12489 Berlin, Germany — ²Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany — ³Department of Biochemistry and Molecular Biophysics, University of Arizona, Tucson, Arizona 85721, United States of America

The primary structural evolution upon electronic excitation of photoactive yellow protein (PYP) in solution has been studied with a combined approach of polarization sensitive ultrafast infrared spectroscopy and density functional theory calculations (Heyne et al., J. Am. Chem. Soc., in press). We identify the $\nu(C_8-C_9)$ chromophore marker mode and show that upon generation of the intermediate I_0 state with a 3 ps time constant a full trans/cis isomerization occurs. Anisotropy measurements of the $\nu(C=O)$ marker mode of Glu46 show that the PYP photoisomerization involves flipping of the enone thioester linkage without significant relocation of the phenolate moiety. Comparison between experiment and theory reveal an important influence of the planarity of the chromophore on the vibrational band patterns. In particular, the chromophore in the dark P state turns out to have a trans geometry with the C=O group slightly tilted out-of-plane, in accordance with an earlier reported structure obtained in an X-ray diffraction study of PYP crystals. In contrast, the I_0 state has a planar configuration.

MO 12.6 Mo 15:30 H12

Multi-Photon Ionization of Molecular Nitrogen by Femtosecond Soft X-ray FEL Pulses — ●MATHIAS RICHTER¹, ANDREI A. SOROKIN^{1,2}, SERGEY V. BOBASHEV², and KAI TIEDTKE³ — ¹Physikalisch-Technische Bundesanstalt, PTB, Abbestrasse 2-12, D-10587 Berlin, Germany — ²Ioffe Physico-Technical Institute, Polytekhnicheskaya 26, 194021 St. Petersburg, Russia — ³Deutsches Elektronensynchrotron, DESY, Notkestrasse 85, D-22603 Hamburg, Germany

At the new free-electron laser (FEL) for vacuum ultraviolet (VUV) and soft X-ray radiation of the Deutsches Elektronensynchrotron (DESY) in Hamburg, multi-photon double ionization of molecular nitrogen was observed and studied by ion time-of-flight spectroscopy. The experiments were performed at the microfocus beamline BL2 of the VUV-FEL with photon pulses of estimated 25-fs duration and irradiance levels up to 20 Terrawatt per square centimeter at a photon energy of 38 eV. Emphasis was laid on the determination of absolute photon numbers per pulse with

the help of a calibrated setup which allows the investigation of non-linear effects by quantitative measurements. Results are discussed in terms of a sequential double photoionization scheme.

MO 12.7 Mo 15:45 H12

A new method for molecule imaging — •TEODORA BAEVA — Institut für theoretische Physik I, Universität Düsseldorf, Germany

Imaging of molecules with sub-angstrom precision and sub-femtosecond resolution is one of the hottest topics in the field of molecule physics at the moment. Two basic methods attract attention : imaging by means of high-harmonics generated by the molecule in a laser field and imaging by means of rescattered electrons, which are ionised by the field and driven back to recollide.

We present a new method for molecule imaging based on the molecule interaction with a single attosecond pulse. We also introduce a new procedure for the effective generation of such pulses by means of laser-overdense plasma interaction and tools for their manipulation.