

DF 9: Focus Session: Structural dynamics in photoexcited molecules

Time: Wednesday 10:00–13:00

Location: H11

Invited Talk DF 9.1 Wed 10:00 H11
Structural dynamics in photoexcited molecules — ●MAJED CHERGUI — Ecole Polytechnique Fédérale de Lausanne

By combining ultrafast optical and X-ray spectroscopies, we can recover the full photocycle of molecular processes in solution. Here we will present two examples, involving the case of ultrafast spin changes in Fe(II)-based molecular complexes, and the case of solvated halides in aqueous solutions.

5 min. break

Topical Talk DF 9.2 Wed 10:40 H11
Ultrafast reversible photogeneration of nitrosyl linkage isomers in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]2\text{H}_2\text{O}$ — ●MATTHIEU NICOL¹, THEO WOIKE¹, and DOMINIK SCHANIEL^{1,2} — ¹I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany — ²CRM2, Université de Nancy, Nancy, France

We report on the photogeneration of nitrosyl linkage isomers in single crystals of sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]2\text{H}_2\text{O}$. Using pump-probe spectroscopy with a time-resolution of 160 fs we show that the photoinduced NO rotation from a linearly bound ground state Fe-N-O to a side-on bound $\text{Fe}\langle\text{N}_\text{O}^{\text{N}}\rangle$ is completed within 1.5 ps. The relaxation after photoexcitation is mono-exponential with a time constant of 300(20) fs, indicating that during the NO rotation no intermediate state with lifetimes longer than 100 fs exists.

Topical Talk DF 9.3 Wed 11:00 H11
Photoinduced isomerization of molecular switches at metal surfaces — ●PETRA TEGEDER — Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin

Molecular switches represent a fascinating class of functional molecules, whose properties can be reversibly changed between different molecular states by excitation with light or other external stimuli. Using surface science concepts like self assembly to align such molecules in a well defined geometry at solid surfaces, new functional properties may arise, which are relevant for different fields like, e.g., molecular electronics, sensing or biocompatible interfaces. For a microscopic understanding of molecular switching at surfaces, it is essential to obtain detailed knowledge on the underlying elementary processes, for instance the excitation mechanism in photoinduced switching.

I will present a case study of a specifically designed azobenzene derivative on a metal surface, namely tetra-tert-butyl-azobenzene (TBA) adsorbed on Au(111), which is so far one of the best studied system for which reversible conformational changes have been demonstrated. The trans/cis-isomerization of TBA is accompanied by reversible changes in the geometrical and electronic structure of the molecules, allowing to gain mechanistic and quantitative insight into the switching process. Our results demonstrate the feasibility of molecular switching at metal surfaces, but also indicate that the switching properties of the surface-bound species are strongly modified by the interaction with a metal substrate.

Topical Talk DF 9.4 Wed 11:20 H11
Light induced conformational changes of retinal proteins — ●HEINZ-JÜRGEN STEINHOFF — Universität Osnabrück, Osnabrück, Germany

Since the discovery of the light driven proton pump bacteriorhodopsin, the scope of microbial rhodopsins has been considerably extended in view of their functional properties as pumps, sensors, and channels. The structures of these membrane proteins are related, and, as we have shown by electron paramagnetic resonance (EPR) spectroscopy in combination with site-directed spin labeling, light induced isomerisation of the retinal chromophore initiates similar conformational changes in the protein scaffold of bacteriorhodopsin and sensory rhodopsin SRII. The light receptor SRII, in complex with the receptor specific transducer, HtrII, is responsible for the negative phototaxis of halobacteria. The talk focuses on time resolved EPR detection of light induced conformational changes of SRII, which reveals unique conformational rearrangements and uncovers the mechanism of the signal transfer from SRII to the associated transducer HtrII.

Invited Talk DF 9.5 Wed 11:40 H11

Ultrafast photochromism of fulgides — ●MARKUS BRAUN^{1,2}, SIMONE DRAXLER², THOMAS BRUST², and STEPHAN MALKMUS² — ¹Institut für Physikalische und Theoretische Chemie, Johann Wolfgang Goethe-Universität Frankfurt, Max von Laue-Strasse 7, 60438 Frankfurt am Main, Germany — ²Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, Ludwig-Maximilians-Universität München, 80538 München, Germany

Pump-probe spectroscopy with fs-time resolution is a powerful tool to elucidate reaction pathways of complex photoreactions. We use pulse sequences to trigger and influence the reaction dynamics of photochromic indolylfulgides [1]. These experiments give deeper insight in the mechanism of the light-induced pericyclic ring-opening/ring-closure reactions for those molecular switches. The pericyclic reactions occur ultrafast without long-lived intermediates and are associated with a definite change of the steady state absorption spectrum. The ground state isomers are thermally stable, which is favourable for distinct applications (memory) [2]. The ultrafast photoreactions are studied by fs-pump-probe spectroscopy in the UV/Vis and the influence of vibrational excess energy (temperature, wavelength, pre-excitation) on the dynamics and yield is investigated [3].

[1] S. Draxler et al., Phys. Chem. Chem. Phys. 11 (2009) 5019-5027

[2] S. Malkmus et al., Adv. Funct. Mater. 17 (2007) 3657-3662

[3] T. Brust et al., J. Photochem. Photobiol. A 207 (2009) 209-216

5 min. break

Topical Talk DF 9.6 Wed 12:20 H11
***Ab-initio* and semi-empirical molecular dynamics studies of photo-isomerisable molecules** — ●JAN BOYKE SCHÖNBORN, OLE CARSTENSEN, and BERND HARTKE — Christian-Albrechts-University Kiel, Germany

Due to the ongoing trend to miniaturization the interest in molecular scale switches is growing fastly. Fulgides and Azobenzenes are promising systems for future applications. The talk is going to present recent theoretical results on the photochemical properties and dynamics of derivatives of the aforementioned molecules. After careful evaluation by comparison to high level *ab-initio* data (CASSCF/CASPT2), different semi-empirical multireference methods have been used in *ab-initio* molecular dynamics simulations to get a deepened understanding of the ultrafast switching processes. Transient spectra covering a wavelength range of 500 nm and a time period of 1500 fs have been simulated, including 3-5 electronically excited states. The excellent agreement of these simulated spectra with the experimental ones allows for a confident interpretation in terms of mechanistic details. An in-depth analysis of the calculated trajectories indicates that even seemingly minor modifications of the functional groups play major roles in the control of the switching dynamics. Possible ways of simulating switchable molecules embedded in bulk soft matter are discussed briefly.

Topical Talk DF 9.7 Wed 12:40 H11
Influence of ligand substitution and dielectric environment on structural dynamics in photoswitchable molecular compounds — ●VOLKER DIECKMANN, SEBASTIAN EICKE, KRISTIN SPRINGFELD, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Barbarastr. 7, D-49069 Osnabrück, Germany

Tuning of photoswitchable molecular compounds by ligand substitution or alteration of the dielectric environment is motivated either to reveal deeper physical insight to the underlying molecular switching mechanisms or the targeted molecular design in various applications such as in biomimetics. In this talk, we highlight our results on: (a) ligand substitution at the example of $[\text{Ru}(\text{bpy})_2(\text{R-OSO})]^+$ solved in propylene carbonate with different ligands R; (b) an altered dielectric environment at sodium nitroprusside compounds electrostatically attached to TiO_2 thin films in comparison to a liquid solution. The impact of these alterations is studied optically by means of time-resolved absorption spectroscopy in the VIS and IR-spectral range, which is related to structural changes upon light-exposure via changes in the molecular polarizability and molecular vibrations. While only slight changes are verified by ligand substitution in the sulfoxide compounds, the photofunctionality of the nitrosyl compound changes dramatically from light-induced linkage isomerization into a photo-release of the NO-bond.

Financial support by the DFG (project GRK 695) is gratefully ac- | knowledged.