

MO 8: Photochemistry

Time: Tuesday 10:30–12:30

Location: V38.02

MO 8.1 Tue 10:30 V38.02

Single-molecule studies of photoswitchable organic triads — ●REGINA SCHMIDT¹, MARTTI PÄRS¹, CHRISTIANE HOFMANN¹, PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We have investigated a triad, consisting of two perylenebisimide (PBI) fluorophores that are covalently linked to a photochromic dithienylcyclopentene (DCP) unit [1]. Converting the DCP between its two isomeric forms allows to modulate the PBI emission intensity of up to 80% of the signal level. Exploiting these features we have demonstrated on the ensemble level the potential of these triads to act as an optical transistor [2]. Here we will communicate our first steps to expand these experiments to the single-molecule level.

[1] M. Irie, *Chem. Rev.* 100, 1685-1716 (2000).

[2] M. Pärns, *Angew. Chem. Int. Ed.* 50, 11405-11408 (2011).

MO 8.2 Tue 10:45 V38.02

Control of photochromic molecules adsorbed to optical microfibres — ●ULRICH WIEDEMANN, WOLFGANG ALT, and DIETER MESCHÉDE — Institut für Angewandte Physik, Universität Bonn, Wegelerstraße 8, 53115 Bonn

The high light intensity on the surface of an optical microfibre can be used for strong light-matter interaction experiments with surface adsorbates. In previous experiments in our group ultra-sensitive absorption spectroscopy of surface-adsorbed organic dye molecules has been demonstrated [1]. After the passive observation of organic dyes, the next level of complexity is the optical manipulation of photochromic molecules. Switching between the molecular states is achieved by exposure to the evanescent field of a few nanowatts of UV or white light guided in the microfibre. The internal state of the molecules is detected via their state-dependent light absorption.

We present a quantitative analysis of the time-resolved photoswitching dynamics, which are measured and mathematically modelled with a rate equation model. By adjusting the microfibre evanescent field strength the dynamic equilibrium state of the molecules is controlled. Finally, we investigate how many times the photochromic system can be switched before undergoing significant photochemical degradation.

[1] F. Warken, E. Vetsch, D. Meschede, M. Sokolowski, and A. Rauschenbeutel, "Ultra-sensitive surface absorption spectroscopy using sub-wavelength diameter optical fibers," *Opt. Express* 15(19), 11952–11958 (2007).

MO 8.3 Tue 11:00 V38.02

Photochromic polypyridine ruthenium sulfoxide complexes on their way to condensed matters — ●KRISTIN SPRINGFELD, VOLKER DIECKMANN, SEBASTIAN EICKE, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Germany

Creating new, more efficient data storage systems brings strong demand for materials that exhibit fast recording processes and long storage times. A promising approach are optical data storage devices that make use of photochromic molecules as storage materials, e.g., ruthenium polypyridine sulfoxides. They offer light-induced linkage isomerization at the SO-ligand accompanied with a pronounced UV/VIS photochromism, a tremendous photosensitivity and high thermal stability of the two metastable isomers. However, the field of applications is limited so far, because only molecular solutions are available. Here, we discuss the characteristic photochromic properties of the compounds in the frame of ligand substitution and replacement of the dielectric environment. The complex $[\text{Ru}(\text{bpy})_2(\text{ROSO})]\cdot\text{PF}_6$ [1] (with OSO: 2-methylsulfinylbenzoate) has been modified with several functional groups and was studied in different solvents as well as immobilized in an inorganic polymer. The analysis is performed by cw-pump-probe technique as a function of temperature and exposure. We discuss the impact of our findings in view of application in molecular photonic devices.

Financial support by the DFG (INST 190/137-1) and the DAAD (50445542) is gratefully acknowledged.

[1] V. Dieckmann et al., *Opt. Express* 17, 15052 (2009)

MO 8.4 Tue 11:15 V38.02

Photoswitchable ruthenium sulfoxides and their adaptability for nonlinear molecular photonics — ●SEBASTIAN EICKE, SERGEJ BOCK, VOLKER DIECKMANN, KRISTIN SPRINGFELD, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Germany

Ruthenium sulfoxides like $[\text{Ru}(\text{bpy})_2(\text{OSO})]^+$ (OSO: 2-methylsulfinylbenzoate) offer a light-induced linkage isomerization located at the SO-ligand resulting in pronounced changes of characteristic optical properties. These photoswitchable molecules are out-standing due to an ultrafast optical response in the ps range and a pronounced photochromism in the visible spectral range as well as long lifetimes in the metastable states. Furthermore, they can be simply tuned via ligand substitutions or different dielectric environments allowing for the adjustment of the spectral addressability, the magnitude of the absorption change and the generation/relaxation rates.

The talk gives a review on various molecule adaptabilities and presents a novel representative of the group of ruthenium sulfoxides whose optical properties have been successfully adjusted to the most common commercial laser sources. Thus the unique spectral addressability, the high efficient and the fast light-induced conversion of this new compound allow for applications in a multiplicity of devices. We particularly discuss their potential for ultrafast optical switches for controlling light by light and next-generation realtime holographic displays.

*Financial support by the DFG (INST 190/137-1) and DAAD (50445542) is gratefully acknowledged.

MO 8.5 Tue 11:30 V38.02

Ultrafast dynamics of photolyzed carbon monoxide in the primary docking site of hemoglobin, FixLH and R220H FixLH — ●PATRICK NUERNBERGER^{1,2}, KEVIN F. LEE¹, ADELINE BONVALET¹, LATIFA BOUZHIR-SIMA¹, JEAN-CHRISTOPHE LAMBRY¹, URSULA LIEBL¹, MANUEL JOFFRE¹, and MARTEN H. VOS¹ — ¹Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, and INSERM U696, 91128 Palaiseau, France — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We report a mid-IR study of the ultrafast dynamics of CO in the docking site of the heme proteins hemoglobin, FixLH and the mutant R220H FixLH. We employ a recently developed chirped-pulse upconversion method that allows for simultaneous measurement of the absorption of both heme-bound and docked CO with high spectral resolution and sensitivity. The bacterial oxygen sensor FixLH displays marked differences in dynamic behavior upon ligand dissociation with respect to hemoglobin. We find that CO bound to the heme iron in FixL is tilted by $\approx 30^\circ$ with respect to the heme normal, which contrasts to the situation in globins and in present FixLH-CO X-ray crystal structure models. This implies protein environment-induced strain on the ligand, which is possibly at the origin of a very rapid docking site population in a single conformation. Our observations likely explain the unusually low affinity of FixL for CO that is at the origin of the weak ligand discrimination between CO and O₂.

MO 8.6 Tue 11:45 V38.02

Photosensitized generation of diphenylmethyl cations — ●SEBASTIAN THALLMAIR^{1,2}, CHRISTIAN F. SAILER¹, JOHANNES AMMER², EBERHARD RIEDLE¹, and REGINA DE VIVIE-RIEDLE² — ¹LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München — ²Department Chemie, Ludwig-Maximilians-Universität München

Carbocations are omnipresent intermediates in organic chemistry as well as in biochemistry. Photoinduced bond cleavage of diphenylmethylphosphonium cations offers a convenient and very effective way to generate diphenylmethyl cations in both polar and moderately polar solvents. An alternative route to the direct photoexcitation is to use a photosensitizer to induce the bond cleavage. We looked at anthracene as a possible candidate.

Its low energy absorption band ($\lambda \approx 360$ nm) is well separated energetically from the absorption bands of the precursor molecule ($\lambda \approx 280$ nm) and therefore gives the possibility to excite anthracene selectively in the presence of diphenylmethylphosphonium cations. Ultrafast broadband transient absorption measurements deliver insight into the evolution of the photoproducts from the femto- to the microsecond

timescale. We can show that carbocations are generated from the S_1 state of anthracene. In contrast, the anthracene triplet seems to be unreactive.

Based on quantum chemical calculations performed for a phosphonium model system the mechanism of photosensitization will be discussed.

MO 8.7 Tue 12:00 V38.02

Towards ion molecule reactions in selected vibrational states

— •FABIAN HOCHHEIMER, MARTIN STEI, EDUARDO CARRASCOSA, ADITYA KELKAR, THORSTEN BEST, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

The S_N2 mechanism is one of the fundamental chemical reaction mechanisms. Using cross beam velocity map imaging our group has verified the long proposed direct S_N2 mechanism in the reaction $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ [1]. The text book picture involves an inversion of the CH_3 umbrella in the transition state [2]. As we could observe an efficient channeling of energy through the molecule, the question arises whether vibrational excitation of the umbrella mode acts as a spectator or influences the reaction. Using an IR-laser to prepare the molecular internal state prior to collision [3] may help to answer such questions. Here we report on our progress towards scattering of vibrationally excited CH_3I and Cl^- .

[1] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J.X. Zhang, W.L. Hase, M. Weidemüller, R. Wester, *Science* 319, 183 (2008)

[2] W. N. Olmstead, J. I. Brauman, *J. Am. Chem. Soc.*, 99 (1977)

[3] W. Zhang, H. Kawamata, K. Liu, *Science* 325, 303 (2009)

MO 8.8 Tue 12:15 V38.02

Photodissoziation von fluorierten Acetonen nach Anregung in den S_1 -Zustand — •THOMAS MICHALAK und FRIEDRICH TEMPS — Christian-Albrechts-Universität, Kiel

Die Photodissoziation von Aceton spielt für die Atmosphäre eine große Rolle, da die gebildeten Acetyl-Fragmente in einer Folgeraktion mit Luft OH-Radikale bilden. Während der wellenlängenabhängige Zerfall für Aceton weitestgehend untersucht ist, fehlen Untersuchungen zu fluorierten Derivaten. In dieser Arbeit wurde daher die Photodissoziation von Monofluoraceton (MFA), 1,1-Difluoroaceton (DFA) und 1,1,1-Trifluoroaceton (TFA) nach Anregung in den $S_1(n\pi^*)$ -Zustand im Wellenlängenbereich $\lambda = 333 - 240$ nm untersucht. Dazu wurde die Photofragment-Geschwindigkeitskartographie verwendet, die Aufschluss über die Energieverteilung der Fragmente und die Art und Anzahl der Dissoziationskanäle liefert. Detektiert wurde das CH_3 -Fragment. Die experimentellen Ergebnisse wurden durch quantenchemische Rechnungen unterstützt.

Der Dissoziationskanal zu $CH_3 + COCH_xF_y$ ist für $\lambda \leq 310$ nm (TFA), $\lambda \leq 300$ nm (DFA, MFA) offen. Analog zum Aceton erfolgt dieser Zerfall nach einem Intersystem Crossing und dem Überwinden einer Potentialbarriere im T_1 -Zustand. Sowohl die Barrierenhöhen als auch die Dissoziationsenergien der Kanäle konnten experimentell ermittelt werden. Wird die Wellenlänge noch weiter erniedrigt, wird ab $\lambda \leq 260$ nm (TFA), $\lambda \leq 275$ nm (DFA, MFA) auch CH_3 aus dem unimolekularen Zerfall des $COCH_3$ -Fragments detektiert, das aus dem primären Dissoziationskanal zu $CH_xF_y + COCH_3$ stammt.