

MO 14: Photochemistry II

Time: Wednesday 14:30–16:00

Location: MO-H6

MO 14.1 Wed 14:30 MO-H6

Studying the photodynamics of a formazan in binary solvent mixtures — ●SVENJA WORTMANN, SYLVIA SCHLOEGLMANN, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg

1,3,5-Triphenylformazan (TPF) contains an azo group and a hydrazone group, of which both can isomerize upon excitation with visible light. Therefore, TPF can exist in different isomeric forms, which can be converted into each other accompanied by a color change of the solution [1,2]. The ratio of the present formazan isomers and their thermal stability are dependent on the solvent environment and the illumination conditions. Thus, we studied the photodynamic behavior of TPF in toluene solution and with additional admixtures of protic and aprotic cosolvents with transient absorption spectroscopy on different time scales. Especially, the thermal back-isomerization around the C=N double bond shows a high sensitivity regarding the binary solvent mixtures. Finally, it was possible to elucidate the role of solvent polarity as well as the impact of hydrogen bonding. Whereas an increased solvent polarity of the binary mixture results in a decreased activation barrier, hydrogen bonding may have the contrary effect on the thermal back-relaxation. Hence, both hydrogen-bond donors and acceptors as cosolvents can slow the isomerization reaction of TPF [3].

[1] R. Kuhn, H.M. Weitz, *Chem. Ber.* **86**, 1199-1212 (1953)

[2] U.-W. Grummt, H. Langbein, *J. Photochem.* **15**, 329-334 (1981)

[3] S. Wortmann, S. Schloeglmann, P. Nuernberger, *J. Org. Chem.* (2021), DOI:10.1021/acs.joc.1c01928.

MO 14.2 Wed 14:45 MO-H6

Transient FTIR spectroscopy after one- and two-colour excitation on a highly luminescent chromium(III) complex —

●PIT BODEN¹, PATRICK DI MARTINO-FUMO¹, GEREON NIEDNER-SCHATTEBURG¹, WOLFRAM SEIDEL², and KATJA HEINZE³ — ¹TU Kaiserslautern, Fachbereich Chemie und Research Center Optimas, Germany — ²University of Rostock, Institute of Chemistry, Germany — ³JGU Mainz, Department of Chemistry, Germany

In this contribution^[1] the electronic and structural properties of a highly luminescent mononuclear chromium(III) complex with polypyridyl ligands are investigated via luminescence and in particular transient step-scan FTIR spectroscopy at different temperatures.

The relative population of two NIR-emissive energetically close-lying electronically excited doublet states strongly depends on the available thermal energy. In a new kind of two-colour step-scan FTIR experiments the population of the long-lived excited states is further modulated via pump/pump/probe (FTIR) and pump/dump/probe (FTIR) schemes. Hereby, the second pump or dump excitation, following the initial UV pump excitation, is stimulated by an NIR laser pulse with the wavelength being set according to the phosphorescence spectrum. The successful establishment of this new technique is an important step towards investigations on further transition metal complexes.

[1] P. Boden, P. Di Martino-Fumo, G. Niedner-Schatteburg, W. Seidel, K. Heinze, M. Gerhards, *Phys. Chem. Chem. Phys.* **2021**, **23**, 13808.

MO 14.3 Wed 15:00 MO-H6

Reversible (photo)chemistry of Cr(0), Mo(0) and W(0) carbonyl complexes — ●SOPHIE STEIGER¹, PIT BODEN¹, PATRICK DI MARTINO-FUMO¹, TOBIAS BENS², DANIEL MARHÖFER¹, BIPRAJIT SARKAR², GEREON NIEDNER-SCHATTEBURG¹, and MARKUS GERHARDS¹ — ¹TUK, FB Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern — ²University of Stuttgart, Institute of Inorganic Coordination Chemistry, Pfaffenwaldring 55, 70569 Stuttgart

This contribution presents the investigations of the photochemical reactivity of chromium, molybdenum and tungsten carbonyl complexes containing a bidentate pyridyl-mesoionic carbene ligand. The photochemical reactivity of these complexes in pyridine, acetonitrile or in a KBr pellet was analysed by rapid-scan FTIR spectroscopy or by recording static FTIR spectroscopy at defined time intervals. Hereby, the carbonyl stretching vibrations represented suitable IR probes. In the dark after excitation, a reverse reaction to the initial species occurs. The influence of the metal centre and the solvent on the kinetics of the reverse reaction in solution and the quantum yield of the initial photochemical reaction were determined.

Quantum chemical calculations were performed for conceivable photoproducts to characterise the underlying reaction. The loss of an axial CO ligand was assigned to the photoproduct in the solid state at low temperature, with subsequent occupation of the vacant coordination site by a solvent molecule in fluid solution. This interpretation simultaneously explains the appearance of a signal of free CO in the FTIR spectra.

MO 14.4 Wed 15:15 MO-H6

Photochemistry of the Benzaldehyde-BCl₃ Complex —

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The excited state properties of α, β -enones can be altered by complexation with a Lewis acid to enable otherwise unaccessible photochemical transformations.[1] After excitation, α, β -enones relax to a triplet state from which subsequent reactions can occur. This $\pi\pi^*$ triplet is stabilized by interaction with a Lewis acid and studies using UV/Vis transient absorption spectroscopy and quantum chemical calculations show that its formation only takes a few picoseconds.[2] We expected this behavior to also occur in the aromatic α, β -enone benzaldehyde when interacting with the Lewis acid BCl₃. Instead, non-adiabatic dynamics calculations showed ultrafast dissociation of a chlorine atom. The resulting benzyl radical could be identified in a theory-guided UV/Vis ultrafast transient absorption experiment and was found to be surprisingly long lived. This led to the discovery of a novel chemical reaction of benzaldehyde which uses the radical chemistry of chlorine.

[1] *Angew. Chem. Int. Ed.* **2018**, **57**, 14338-14349.

[2] *Angew. Chem. Int. Ed.* **2021**, **60**, 10155-10163.

MO 14.5 Wed 15:30 MO-H6

Accurate determination of the Adenine-Thymine binding energy — ●SEBASTIAN HARTWEG¹, MAJDI HOCHLAF², GUSTAVO GARCIA³, and LAURENT NAHON³ — ¹Albert-Ludwigs-Universität Freiburg, Deutschland — ²Université Gustave Eiffel, Champs-sur-Marne, Frankreich — ³Synchrotron SOLEIL, St-Aubin, Frankreich

Among the many intermolecular interactions known between biomolecules, the hydrogen bonding between the nucleobases Adenine (A) and Thymine (T) as well as between Guanine and Cytosine take a special place since they shape the DNA double strand structure. The strength of these hydrogen-bond interactions, at the center of the genetic code, is thus of significant interest for radiobiology.

We will present a study of the single photon ionization of gas phase A and T molecules and their dimers AA, AT and TT using double imaging photoelectron photoion coincidence (i2PEPICO) spectroscopy performed at the VUV beamline DESIRS of the French SOLEIL synchrotron. By evaluating the threshold photoelectron spectra (TPES) and photon energy-dependent ion kinetic energy release data we determined the threshold for photoionization and dissociative photoionization of the different clusters. By comparison with high-level ab initio calculations dealing with neutral and ionic species, we can relate the determined quantities to the binding energy of the neutral AT pair. The favorable comparison between theory and experimental results gives further credibility in theoretical predictions for similar systems.

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MO 14.6 Wed 15:45 MO-H6

Exciton Diffusion in Perylene Derivative Microcrystals —

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Improving light harvesting and opto-electronic organic devices relies on our knowledge about the transport mechanism of electronic excitations. The transport efficiency of excitons in molecular systems is strongly influenced by the order of the molecules. Amorphous and crystalline structure represent two extreme cases. In this work, we

investigate the exciton dynamics in single organic microcrystals consisting of Perylene Red, a member of the perylene bisimide dye class and exploited already in many applications. We characterize the absorption, emission and geometric properties of single crystals in order to get a detailed view of the intermolecular coupling and the exciton distribution inside an irradiated crystalline sample. X-ray structure analysis reveals an orthorhombic unit cell with a volume of 12 nm^3

consisting of eight dye molecules. Spatially resolved time-correlated single photon counting at high excitation powers is used to extract the diffusion properties of the excitons from two-exciton interaction. We find, that the excitons are indeed mobile within the sample and their motion can be described by an incoherent 'hopping' process. The diffusion length is about 12 nm.