

## MO 2: Photochemistry

Time: Monday 11:00–13:00

Location: F142

## MO 2.1 Mon 11:00 F142

**Time-resolved transient absorption spectroscopy of oxindole-based molecular motors and switches** — ●CAMILO GRANADOS<sup>1,2</sup>, MATTHEW MGBUKWU<sup>2</sup>, DAN DOELLERER<sup>3</sup>, DAISY POOLER<sup>3</sup>, ALINA KHODKO<sup>1,4</sup>, BEN L. FERINGA<sup>3</sup>, JÉRÉMIE LÉONARD<sup>2</sup>, OLEG KORNILOV<sup>1</sup>, and STEFAN HAACKE<sup>2</sup> — <sup>1</sup>Max Born Institute, Max-Born-Straße 2A, 12489 Berlin, Germany — <sup>2</sup>Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, F-67034 Strasbourg, France — <sup>3</sup>Stratingh Institute for Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands — <sup>4</sup>Institute of Physics NAS of Ukraine, Nauky Ave, 46, 03028, Kyiv, Ukraine

The design and characterization of synthetic molecules (motors and switches) is of vital importance for the construction of larger artificial structures that can be used for harvesting light energy and for other light-induced functionality [1]. However, the isomerisation quantum yields of the existing synthetic systems [1], are still low compared to the natural chromophores. Time-resolved transient absorption spectroscopy (TAS) can map the evolution of the relaxation of the molecule along the potential energy surfaces [1] and reveal the mechanisms affecting the isomerisation quantum yields. We will present recent TAS experiments on oxindole-based molecular motors and switches dissolved in different solvents. We will further present plans to investigate these synthetic molecular systems using TRPES. [1] DRS Pooler et. al., Chem. Sci., 12, 7486 - 7497 (2021).

## MO 2.2 Mon 11:15 F142

**Unraveling the photochemistry of  $Ti^{IV}(Cp)_2(NCS)_2$**  — ●JONAS SCHMIDT, LUIS IGNACIO DOMENIANNI, and PETER VÖHRINGER — University of Bonn, DE

Recently, the complex,  $Cp_2Ti(Cl)_2$ , has been used as a photo-redox-catalyst for atom economical transformations in one-electron steps.[1] We investigated the initial excitation and quenching of the catalyst using time-correlated single-photon-counting and femtosecond ultraviolet-pump mid-infrared-probe spectroscopy (UVmIR). The chlorido ligands were substituted with isothiocyanato ligands to render the catalyst amenable to UVmIR.

We recorded the emission spectrum and determined luminescence lifetimes of  $Cp_2Ti(NCS)_2$  in liquid tetrahydrofuran solution at room temperature. The bi-exponential nature of the luminescence decay is highly indicative of thermally activated delayed fluorescence in addition to prompt fluorescence from the optically prepared singlet excited state. The triplet state was successfully quenched with triphenylamine and a Stern-Vollmer quenching constant of  $9.4 \times 10^9 \frac{L}{mol \cdot s}$  was determined

UVmIR data obtained continuously from 50 femtoseconds to several microseconds supported this interpretation and the vibrational signatures of the  $S_1$ - and  $T_1$ -states were obtained by performing a target analysis of the time- and frequency-dependent pump-probe data set.

**References:**

[1] Z. H. Zhang et al., *Angew. Chem. Int.* **2020**, *59*, 9355–9359.

## MO 2.3 Mon 11:30 F142

**Ultrafast Photochemistry of Metallo-Nitrenes** — ●MARKUS BAUER<sup>1</sup>, TILL SCHMIDT-RÄNTSCH<sup>2</sup>, LUIS DOMENIANNI<sup>1</sup>, SVEN SCHNEIDER<sup>2</sup>, and PETER VÖHRINGER<sup>1</sup> — <sup>1</sup>Clausius Institut für physikalische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Deutschland — <sup>2</sup>Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Deutschland

Metallo-nitrenes, formed by the photochemical decomposition of metallo-azides, have recently shown to be promising complexes for chemical catalysis, specifically for nucleophilic metallo-nitrene C-H insertion.[1] The exact reaction pathways, as well as the electronic structures of intermediate species remain so far largely unknown.

In this work, the photochemistry of the square-planar  $[M(N_3)(PNP)]$  ( $PNP=N(CH_2CH_2Bu)_2$ ,  $M=Pd, Pt$ ) complexes after excitation with 320 nm light were investigated using ultrafast UV-pump mIR-probe and time resolved Fourier transform IR-spectroscopy.

The data reveal that dinitrogen cleavage from the photolabile azide group occurs from the triplet state on a time scale in excess of 1 ns. The quantum yield for nitrene formation depends on the nature of the

metal.

[1] T. Schmidt-Räntsch, H. Verplancke, J. N. Lienert, S. Demeshko, M. Otte, G. P. Van Trieste, K. A. Reid, J. H. Reibenspies, D. C. Powers, M. C. Holthausen, S. Schneider, *Angew. Chem. Int. Ed.* **2022**, *61*, e202115626;

## MO 2.4 Mon 11:45 F142

**Photodynamics of arylazopyrazole derivatives: new insights from molecular dynamics studies** — HELENA OSTHUES, ●MARCUS BÖCKMANN, and NIKOS DOLTSINIS — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, Münster, Germany

In the realm of photoswitches, azobenzene is an archetype for studying photodynamics primarily due to its fatigue resistance, simplicity, and tuneability by substitutions at the phenyl rings [1]. Here, we could demonstrate that the time scale of photoisomerisation can be drastically changed upon chemical modification [2]. Recently, the discovery of quantitative arylazopyrazole (AAP) photoswitches with long thermal lifetimes has pushed into focus this class of azobenzene derivatives, where one phenyl ring is replaced by a less bulky five-membered ring [3]. In this contribution, we report on dynamical photoisomerisation simulations of AAP derivatives elucidating the effect of different substituents and solvents on nonradiative lifetimes [4].

[1] H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.* **41**, 1809-1825 (2012).

[2] M. Böckmann, N. L. Doltsinis, and D. Marx, *J. Chem. Phys.* **137**, 22A505 (2012).

[3] L. Stricker, M. Böckmann, T. M. Kirse, N. L. Doltsinis, and B. J. Ravoo, *Chemistry - A European Journal*, **24**, 8639-8647 (2018).

[4] H. Osthues and N. L. Doltsinis, *J. Chem. Phys.* in press.

## MO 2.5 Mon 12:00 F142

**Multireference Chlorophyll Nuclear and Electron Q-Band Dynamics: a Theoretical XAS Study** — ●LENA BÄUML, SEBASTIAN REITER, FLORIAN ROTT, BASTIAN MICHELS, and REGINA DE VIVIE-RIEDEL — Department of Chemistry, LMU Munich, Germany

Chlorophylls play a vital role during photosynthetic light-harvesting. Here, the nonradiative relaxation of high-energy excited states to the lowest excited state is of central importance.

We simulate the ultrafast relaxation process in the Q-bands of chlorophyll in a representative 2D space using grid-based wave packet quantum dynamics. The excited state energies and potential energy surfaces are computed at the XMS-CASPT2 level of theory to capture the multi-reference character of chlorophyll excitations. We propose a possibility to observe the wave packet dynamics, as well as the strong coupling between the  $Q_x$  and  $Q_y$  state via magnesium K-edge X-ray absorption spectra. Following the RASPT2 procedure outlined by Rott *et al.*[1] our results show from a fully quantum mechanical point of view how the  $Q_x$  and  $Q_y$  band are strongly coupled by internal vibrations,[2] in contrast to the Gouterman model. Thus the absorption intensity should be spread over the whole Q-band, influencing charge and energy transfer in photosynthetic light-harvesting complexes, such as photosystem 1.

[1] F. Rott *et al.*, *Struct. Dyn.*, **8**, 034104 (2021).

[2] L. Bäuml *et al.*, *Phys. Chem. Chem. Phys.* **24**, 27212 (2022).

## MO 2.6 Mon 12:15 F142

**The role of dephasing for dark states and polaritonic chemistry** — ●ERIC DAVIDSSON and MARKUS KOWALEWSKI — Department of Physics, Stockholm University, Albanova University Center, SE-106 91 Stockholm, Sweden

Common quantum-mechanical models for chemistry in optical cavities lack a mechanism to populate collective dark states. In this work, we explicitly model a process that does populate these states; i.e. disorder from loss of phase information (decoherence) in the matter sub-systems. Such processes arise due to local environment interactions, and the effect enters into the equations of motion as dephasing operators. Viewed through the lens of polaritonic states, a reservoir of previously inaccessible states has thus opened up. Since these states are superpositions of excitations in only matter sub-systems, one would expect that dephasing can protect excited states from photon decay. In this work, we find that dephasing indeed does that quite effectively.

We also discuss how to understand the same physical result in a standard product basis, where there are no dark states.

MO 2.7 Mon 12:30 F142

**Cavity-induced effects on the ground-state chemical reactivity of the click reaction** — •THOMAS SCHNAPPINGER and MARKUS KOWALEWSKI — Department of Physics, Stockholm University, Sweden

If a molecule interacts with the vacuum field of a nanoscale cavity, strong coupling reshapes the potential energy surfaces, forming hybrid light-matter states, termed polaritons. Recent experiments show that this strong coupling between light and matter is capable of modifying chemical and physical properties. The situation in which the quantized cavity modes are coupled via their characteristic frequency to vibrational degrees of freedom of molecules is called vibrational strong coupling (VSC). In the VSC regime, the chemistry of a single electronic state (mostly the ground-state) and its vibrational spectroscopy are influenced by the cavity interaction.

In this theoretical contribution, we study different aspects to see to what extent and how the chemical reactivity can be altered by VSC in the single-molecule case. As an illustrative example, we are investigating the azide-alkyne Huisgen cycloaddition, which is better known as the prototypical click reaction. We describe the hybrid light-molecule matter system with the help of an extended Jaynes-Cummings-like

model taking into account the counter-rotating terms and the dipole-self-energy terms. In this setup, we can realize coupling to multiple cavity modes and study the cavity-induced changes of ground-state energies, geometries, and activation energies.

MO 2.8 Mon 12:45 F142

**Suppressing non-radiative decay of photochromic organic molecular systems in the strong coupling regime** — •MARKUS KOWALEWSKI and RAFAEL C. CUOTO — Stockholm University, Stockholm, Sweden

Organic solar cells and related optoelectronic applications rely on molecules with long-lived electronic states. Non-radiative decay channels, which are caused, for example, by non-adiabatic processes in the molecule can have a significant impact on the efficiency of these devices. More favorable lifetimes are in practice, achieved by chemical substitution of particular base compound.

In this contribution, we investigate meso-tert-butyl-BODIPY, which is known for its low fluorescence yield, caused by the non-radiative decay through a conical intersection [1]. We show theoretically that strong light-matter coupling by means of an optical nano-cavity may be used to modify the excited state lifetime.

[1] R. C. Couto, M. Kowalewski, Phys. Chem. Chem. Phys., **24**, 19199 (2022).