

MO 8: Fast Intramolecular Dynamics

Time: Tuesday 14:30–16:30

Location: N 25

Invited Talk

MO 8.1 Tue 14:30 N 25
Ultrafast dynamics of a magnetically bistable molecular switch by fs transient absorption spectroscopy — ●SEBASTIAN MEGOW¹, JULIA BAHRENBURG¹, HENDRIK BÖHNKE¹, MATS BOHNSACK¹, MARK DITTNER¹, MARCEL DOMMASCHK², RAINER HERGES², and FRIEDRICH TEMPS¹ — ¹Institute of Physical Chemistry, Christian-Albrechts-University, Max-Eyth-Strasse 1, 24098 Kiel, Germany — ²Otto-Diels-Institute of Organic Chemistry, Christian-Albrechts-University, Otto-Hahn-Platz 6/7, 24098 Kiel, Germany

The phenylazopyridine (PAP)-functionalized Ni-porphyrin-based molecular switch, dubbed "record player" (RP), has recently drawn considerable attention as it shows magnetic bistability at room temperature in homogeneous solution upon irradiation [Venkataramani *et al.*, *Science* **331** (2011)]. The reversible photoswitching process between the diamagnetic low- and the paramagnetic high-spin compound occurs under isomerization and (de-)coordination of the PAP moiety. Surprisingly, the spin-crossover seems to be triggered by absorption in the porphyrin macrocycle rather than photoisomerization of the PAP. To shed light on the underlying mechanism, we have monitored the ultrafast dynamics of the *cis*- and *trans*-PAP RP by means of fs transient absorption spectroscopy after photoexcitation. While the low-spin compound shows virtually identical dynamics to pure Ni-porphyrin without formation of any identifiable spin-switching product, the high-spin compound shows formation of the low-spin product within 12 ps with an estimated quantum yield of $6 \pm 1\%$.

MO 8.2 Tue 15:00 N 25
Time-Resolved Spectroscopy of the Molecular Rotor Thioflavin T and its Building Blocks — ●BASTIAN GEISSLER, PHILIPP GERSCHEL, ANNA LISA SEMRAU, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Thioflavin T (ThT) is a benzothiazole salt linked to N,N-dimethylaniline. ThT is widely used as a marker for biophysical studies on the misfolding and aggregation of proteins. The spectroscopic properties of ThT depend on the freely rotatable bond between the benzothiazole and the aniline moieties. The associated rotation is the main (non-radiative) depopulation channel of the excited state, which has a lifetime well below 10 ps [1,2]. The fluorescence behavior of ThT exhibits a pronounced dependence on the excitation wavelength, attributed to the pre-rotation angle of the ground-state molecule [3].

We perform time-resolved spectroscopy via fluorescence upconversion, TCSPC and transient absorption for ThT and its building blocks. Depending on the excitation wavelength, fluorescence and excited-state dynamics drastically change, shifting from ps to ns. A comparison of ThT and benzothiazole confirms that for near-UV excitation, the ThT dynamics solely originate from a pre-rotated subensemble for which the two building blocks are spectroscopically independent and no excited-state depopulation through rotation occurs. Hence, our studies provide a time-domain corroboration of the pre-rotation model [3].

[1] V. Stsuapura *et al.*, *J. Phys. Chem. A* **114**, 8345–8350 (2010).

[2] I. Kuznetsova *et al.*, *Anal. Chem.* **88**, 718–724 (2016).

[3] S. Freire *et al.*, *Dyes Pigm.* **110**, 97–105 (2014).

MO 8.3 Tue 15:15 N 25
Quantum chemical studies of a hemithioindigo-based photo-driven molecular motor — ●FLORIAN ROTT, SVEN OESTERLING, and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München
 In recent years photodriven molecular motors got increasing interest due to their ability to convert light energy into directional motion and thus providing energies of future nanomachines.

Dube *et al.* [1] synthesised a hemithioindigo-based photodriven molecular motor. This motor performs a full rotation after excitation with visible light, showing > 95% unidirectionality at a very fast rate of 1 KHz at 20°C. The full rotation is believed to be a three step process consisting of two light induced and one thermal step.

However, the mechanism accounting for the rotation is not completely understood. To elucidate the reaction path we performed excited state quantum chemical calculations at the CASSCF level of theory. Several conical intersections are involved in the light-induced process and enables the fast rotation of the molecular motor.

[1] M. Guentner, M. Schildhauer, S. Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, *Nat. Commun.* **6**, 8406 (2015).

MO 8.4 Tue 15:30 N 25
Femtosecond dynamics of the 2-methylallyl radical in the gas phase — ●ANJA RÖDER¹, INGO FISCHER¹, ROLAND MITRIC¹, JENS PETERSEN¹, KEVIN ISSLER¹, MATTHIAS WOHLGEMUTH¹, and LIONEL POISSON² — ¹University of Wuerzburg, Am Hubland Süd 97074 Wuerzburg, Germany — ²LIDYL, CEA, CNRS, Université Paris-Saclay, CEA Saclay, F-91191 Gif-sur-Yvette, France

The methylated derivatives of the allyl radical (the 1-methylallyl or 2-methylallyl radical) are especially interesting for combustion chemistry, since biodiesel often contains branched or non-branched unsaturated fatty esters.

Produced via pyrolysis, the 2-methylallyl radical was examined using femtosecond pump-probe spectroscopy, with the pump laser wavelengths at 240 and 236 nm exciting into a p-state. The probe laser was the 800 nm fundamental of a Ti:Sapphire Laser. The lifetimes of these states were examined using time-resolved photoelectron spectroscopy (TRPES) or time-of-flight mass spectrometry (TOF-ms), showing two time-constants and considerable anisotropy in the photoelectron spectra.

Molecular-dynamic calculations using the field-induced surface hopping method coupled to DDFT reproduce well our experimentally result. The excited p-state decays faster than the time-resolution of the pump-laser to the 3s-state, which decays via the D1-state (first time constant) to the electronic ground state. (Second time constant) This assignment is further supported by the strong positive anisotropy in the photoelectron images, in agreement with ionization from an s-orbital.

MO 8.5 Tue 15:45 N 25
Time-resolved fluorescence studies of a polycyclic tetrazolium compound in solution — ●TOM BOLZE, JAN-LUCAS WREE, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Tetrazolium salts are usually colorless and non-fluorescent, whereas the closely related formazans exhibit a bright range of colors. Since reduction of tetrazolium compounds often leads to formazans, numerous applications have been developed that exploit the color change. However, also photo-oxidation can occur, so that e.g. phenyl-benzo[c]tetrazolo-cinnolinium (PTC), one of the very few known fluorescent tetrazolium compounds, is formed from triphenyl-tetrazolium chloride (TTC) upon irradiation with ultraviolet (UV) light in alcoholic solution.

We investigate the fluorescence dynamics of PTC using time-correlated single-photon counting (TCSPC) and femtosecond fluorescence upconversion. PTC is first generated photochemically by UV excitation of TTC at 265 nm. Our TCSPC results in ethanol disclose an excited-state lifetime of ≈ 700 ps for PTC after S_1 excitation and further indicate additional dynamics on an ultrafast time scale. As is evident in fluorescence upconversion measurements, these faster dynamics occur with a characteristic time constant of 6 ps for S_1 excitation, whereas this time constant is significantly longer for S_2 excitation, presumably reflecting the dissipation of different amounts of excess energy. Studies in more viscous solvents complement the results, and reaction pathways of excited PTC beyond the radiative one are discussed.

MO 8.6 Tue 16:00 N 25
Long-lived coherence with multiple vibrational frequencies in pentafluoropyridine as a probe of $\pi\pi^*$ - $\pi\sigma^*$ vibronic coupling — ●JONAS ANDREAS KUS, OLE HÜTER, and FRIEDRICH TEMPS — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

The electronic structure of pyridine changes significantly when the hydrogen atoms are substituted by fluorine. Due to the high electronegativity of fluorine, the $\pi\sigma^*$ state is energetically lowered. This so-called perfluoro effect enables vibronic coupling of the $\pi\sigma^*$ state with the lower-lying $\pi\pi^*$ state. Using femtosecond time-resolved time-of-flight mass spectrometry after excitation at $\lambda = 255$ nm, we observed multiple oscillations of the ion yield which can be attributed to the vibronic coupling. A pronounced oscillation at a frequency around $\nu = 60$ cm^{-1} is superimposed by several oscillations of higher frequency. From results of femtosecond photoelectron imaging spectroscopy, we can rule

out population transfer from the initially excited $\pi\pi^*$ state to a different electronic state. Supported by quantum chemical calculations at the RI-SCS-CC2, CASSCF and XMCQDPT2 levels of theory, we suggest a strong distortion of the initially excited $\pi\pi^*$ state by the coupling to the higher-lying $\pi\sigma^*$ state. The wavepacket motion in the anharmonic double well potentials modulates the ionization probability, thereby causing the observed oscillations. Taking into account our recent result for pentafluorobenzene [Hüter *et al.*, JCP **145** (2016)], strong $\pi\pi^*$ - $\pi\sigma^*$ vibronic coupling seems to have an important general influence on the excited-state dynamics of perfluorinated aromatics.

MO 8.7 Tue 16:15 N 25

L_a or L_b, that is the question! – A quantum dynamical study of pyrene — •MATTHIAS K. ROOS, SEBASTIAN REITER, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Pyrene, the textbook example for the formation of excimers, is nowadays a widely used fluorescence marker, sensing molecule and building

block in organic semiconductors useful for organic lightemitting diodes (OLEDs) or organic photovoltaic cells (OPV). Nonetheless, the basic mechanism behind its exceptional photophysics is not well understood.

Pyrene is excited by UV light to the S₂ state, a $\pi\pi^*$ state labeled L_a according to Platt's notation. Meanwhile, S₁ or L_b only has a negligible contribution to the absorption due to cancellation effects. Yet, emission occurs exclusively from the L_b state according to experiments. Therefore, an ultrafast relaxation pathway like a conical intersection between these two states must exist.

We use quantum dynamical methods to simulate this photophysical process on a two dimensional grid, built from displacement vectors between minimum structures. Therefore, we employ the Wilson G-Matrix method for the kinetic energy operator. The quantum chemical potential is dealt with a state of the art post-HF method. Couplings between excited potential energy surfaces result from diabaticization. We discuss wave packet evolution, population transfer and distribution. The delay time is compared to experimental results and we talk about the implications of our simulation.