

MO 11: Photochemistry

Time: Wednesday 10:30–12:30

Location: S HS 001 Biologie

Invited Talk MO 11.1 Wed 10:30 S HS 001 Biologie
Properties of multiazobenzene systems - old dogs and new tricks — ●CHAVDAR SLAVOV¹, CHONG YANG², LUCA SCHWEIGHAUSER³, ANDREAS H. HEINDL³, TIM STAUCH², HERMANN A. WEGNER³, ANDREAS DREUW², and JOSEF WACHTVEITL¹ — ¹IPTC, Goethe University, Frankfurt, Germany — ²IWR, University of Heidelberg, Heidelberg, Germany — ³IOC, Justus Liebig University, Giessen, Germany

Azobenzenes (AB) are extensively used in the development of photo-switchable nanostructures. While the photochromism of single ABs is studied in detail, the behavior of connected ABs is not well understood. We combine ultrafast spectroscopy and quantum chemical calculations to explore the properties of different multi-AB constructs [1-4]. The arrangement and the interactions of the individual photoswitch units alter the photochemistry of these systems and give rise to a variety of new molecular properties - intramolecular excitonic coupling, extended π -delocalization, molecular strain, etc. Based on our results, we conceptualize a single-molecule triple photoswitch, with selectively addressable units [4]. Such a system can be used in functional nano-materials as a hub integrating the response to different signals. In the light of the wide spread construction and utilization of photoresponsive compounds, our studies bring new and important insights.

- [1] C. Slavov, et al., PCCP, 18, 14795 (2016)
- [2] C. Slavov, et al., ChemPhysChem, 18, 2137 (2017)
- [3] C. Slavov, et al., JPC Lett., 9, 4776 (2018)
- [4] C. Yang, et al., Chem. Sci, DOI: 10.1021/acs.jpcclett.8b02159

MO 11.2 Wed 11:00 S HS 001 Biologie
Azobenzene isomerization probed by photon spectroscopy — ●MARIO NIEBUHR¹, ANDRÁS BÓDI², PATRICK HEMBERGER², FABIANO LEVER¹, DENNIS MAYER¹, JAN METJE¹, MATTHEW ROBINSON¹, DOMENIK SCHLEIER³, INGO FISCHER³, and MARKUS GÜHR¹ — ¹Institute for Physics and Astronomy, Uni Potsdam, Germany — ²VUV Spectroscopy Group, PSI, Switzerland — ³Institute for Physical and Theoretical Chemistry, Uni Würzburg, Germany

Azobenzene's characteristic trans-cis isomerization, a fully reversible and esp. UV/Vis excitable process, is a good model system for photo-addressable molecular switches. While the molecule itself and its derivatives are well on their way from purely scientific interest towards real-world applications, the underlying isomerization mechanics are still being researched. Prominent examples are the intermediate molecular geometries while switching between the two isomeric states or in our case the Kasha rule violation observable in the trans and cis isomerization yield after excitation to the S_1 resp. S_2 state.

We will present first findings from combining ultra-fast UV pump-probe ion time-of-flight spectroscopy with quasi-cw, synchrotron based VUV fragmentation studies on isolated azobenzene molecules in the gas phase. Former yields time dependent information on form and distance between electronic levels while the later allows us to deduce the initial excited state of the parent molecule from the observed fragments. Thus, we get a better image of the ionic states involved in the itof experiment to characterize and understand the relaxation pathway during the isomerization process.

MO 11.3 Wed 11:15 S HS 001 Biologie
Time-dependent mass spectra studies of gas-phase trans-stilbene oxide as probed by ultrafast UV pump-probe laser techniques — ●MATTHEW S. ROBINSON, MARIO NIEBUHR, and MARKUS GÜHR — Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany.

The photo-chemical ring-opening mechanisms of oxirane-based molecules are heavily dependent on the substituent groups attached to the molecule. Photo-excited unsubstituted and alkyl-substituted oxiranes favor cleavage of the C-O bond, whilst cyano- and aryl-substituted oxiranes cleave at the C-C bond and open in disrotary fashion, in agreement with Woodward-Hoffman rules. [1]

However, in direct contrast to these rules, theory predicts that there is no favored route between the conrotary and disrotary opening paths of photo-excited aryl-substituted oxiranes, despite the conrotary motion rarely being observed. [2] In order to better understand these systems we have performed time-resolved UV pump-probe mass spectra studies on gas-phase trans-stilbene oxide (trans-2,3-diphenyloxirane).

Here we present the results from these experiments, detailing information on the lifetimes of the observed fragments, as well as what this informs us about the photo-excited state of stilbene oxide.

1. Woodward, R. B. & Hoffmann, R., Angew. Chemie 81, 797-870 (1969).
2. Friedrichs, J. & Frank, I. Chem. - A Eur. J. 15, 10825-10829 (2009).

MO 11.4 Wed 11:30 S HS 001 Biologie
Tuning Excited-State Proton Transfer of a Super-Photoacid — ●NIKLAS SUELZNER¹, BASTIAN GEISSLER¹, ALEXANDER GRANDJEAN², GREGOR JUNG², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Biophysikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken

Special molecules, referred to as photoacids, exhibit an acidity increase upon irradiation. Triggered by photoexcitation, such molecules perform an excited-state proton transfer (ESPT) if suitable proton acceptors are present. Moreover, super-photoacids, i.e. with a negative pK_a value in the excited-state, are even strong enough for ESPT in non-aqueous solution. In previous studies, we observed ESPT from the neutral, super-photoacidic HPTS-derivative hydroxypyrenetris(hexafluoropropanylsulfonate) to acetone. However, the influence of water on ESPT in this aprotic environment remained unresolved.

The present study investigates the ESPT kinetics of this photoacid in binary acetone-water mixtures by time-resolved fluorescence spectroscopy on the picosecond timescale. Owing to the fluorescence of both the protonated and deprotonated species, information on ESPT is hereby directly accessible through the fluorescence dynamics. First, we reveal the severe effect of water in the mixtures constituting in an acceleration of ESPT with increasing concentration. Afterward, we demonstrate that the water-driven acceleration can be antagonized by adding an excess of strong acid. Based on this, we infer that strong acids can be used to effectively deactivate water towards ESPT.

MO 11.5 Wed 11:45 S HS 001 Biologie
Steering proton transfer pathways of the bifunctional photoacid 7-hydroxyquinoline — ●MARIUS-ANDREI CODESCU and ERIK T. J. NIBBERING — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, 12489 Berlin

Acid-base neutralization reactions in protic solvents typically occur through proton exchange pathways consisting of a solvent bridge connecting acid and base. Bifunctional photoacids have both proton donating and accepting sites, enabling real-time probing of proton exchange through a well-defined number of solvent molecules. For 7-hydroxyquinoline (7HQ), compelling evidence pointed to initial proton abstraction by the quinoline N site from the methanol solvent, followed by methoxide transport to the OH-site, making it a proton hole transport [Hoffmann et al., J. Phys. Chem. A 120, 9378 (2016)]. This strongly contrasts to the generally accepted picture of an excess proton transport pathway initiated at the OH-site. Here we show that by adding formate anion to 7HQ in methanol, the dominant proton transport pathway of 7HQ changes from a transmission of proton holes to that of excess protons. We follow the reaction dynamics by probing IR-active marker modes of 7HQ and of formic acid with femtosecond time resolution, and determine the local parameters that open up the excess proton transport route. Our findings may provide insight into proton transport pathways of transmembrane proton channel proteins.

MO 11.6 Wed 12:00 S HS 001 Biologie
Ultrafast dissociation of vinyl bromide after passage through a conical intersection: an experimental and theoretical study — FLORIAN ROTT¹, MAURIZIO REDUZZI^{2,3}, ●THOMAS SCHNAPPINGER¹, STEPHEN R. LEONE^{2,4,5}, and REGINA DE VIVIE-RIEDLE¹ — ¹Department of Chemistry, LMU Munich, Germany — ²Department of Chemistry, University of California, Berkeley, USA — ³ICFO - The Institute of Photonics Sciences, The Barcelona Institute of Science and Technology, Spain — ⁴Chemical Sciences Division, Lawrence Berkeley National Laboratory, USA — ⁵Department of Physics, University of California, Berkeley, USA

The ultrafast dissociation of vinyl bromide after strong-field excitation is characterized experimentally and theoretically. After a multiphoton

excitation of the $\pi\pi^*$ transition, the relaxation process is illuminated via Attosecond Transient Absorption Spectroscopy (ATAS) using the bromine M-edge. This method allows to monitor the evolution of the nuclear wave packet during the dissociation of bromine within 100 fs.

Using non-adiabatic molecular dynamics in combination with high-level multi-reference methods we are able to simulate the corresponding time-dependent transient absorption spectrum of vinyl bromide. The simulated spectrum shows a good agreement with the experimental ATAS trace in the relevant energy range.

This joint experimental and theoretical work provides insight into the nuclear dynamics of dissociating vinyl bromide.

MO 11.7 Wed 12:15 S HS 001 Biologie

Controlling the dynamics of the photodissociation of diphenylmethyl bromide — •FRANZISKA SCHÜPPEL, MATTHIAS K. ROOS, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Carboradicals and -cations are key intermediates for many chemical reactions and can be generated by UV-laser excitation from certain precursor molecules. Recently, we investigated the photodissociation of diphenylmethyl bromide using quantum dynamics simulations. [1] The dynamics is characterized by two consecutive conical intersections (CoIns) with the first one leading to the favored homolytic dissociation channel.

The control of the ratio of homolytic and heterolytic bond cleavage is of major interest for chemical applications. By using a second few-cycle IR laser pulse it is possible to create a superposition of a wave packet at a CoIn and by that control the population transfer through that CoIn. [2] We want to apply such a laser pulse to diphenylmethyl bromide to explore to which extend the population transfer of the wave packet through the first CoIn can be disabled. By that we want to regulate the branching between carbocation and carboradical formation.

[1] F. Schüppel *et al.*, *PCCP* **20** (2018), 22753-22761.

[2] P. von den Hoff *et al.*, *PCCP* **14** (2012), 14460-14485.