MO 8: MO Poster 2

Time: Tuesday 17:00–19:00

Location: Empore Lichthof

in solution [3]. Furthermore, we analyze the arrangement of chiral surfactants around the achiral dye Congo red and the ultrafast change in chirality after excitation.

[1] A. Steinbacher, et al., Opt. Express 25, 21735 (2017)

[2] S. Dal Conte, et al., Phys. Rev. B 92, 235425 (2015)

[3] C. Kaufmann, et al., J. Am. Chem. Soc. 140, 31, 9986 (2018)

MO 8.4 Tue 17:00 Empore Lichthof Ultrafast processes in Ru(II)-Au(I)-complexes bridged via paracyclophane with varying metal-metal-distances — •LARS Schüssler¹, ROUMANY ISRAIL², MARCEL SCHMITT², CHRISTOPH ZIPPEL³, DANIEL M. KNOLL³, STEFAN BRÄSE³, CHRISTOPH RIEHN², and ROLF DILLER¹ — ¹Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern — ³Dept. of Org. Chem., KIT, 76131 Karlsruhe

The novel complex [Ru(bpy)₂(ppy)-PCP-(PPh₂)AuCl]⁺ (1) (bpy = 2,2'-bipyridine, ppy = 2-phenylpyridine, PCP = paracyclophane, PPh₂ = diphenylphosphine) [1] - where a Ru(II)-antenna-unit is bridged via PCP to a catalytically active Au(I)-unit - is perfectly suited to systematically investigate the electronic communication between the two metal centers by tuning their distance and the electronic coupling via structurally diverse PCP-bridges (binding sites at the PCP unit, e.g. pseudo-para-position with longer metal-metal-distance as compared to pseudo-ortho-position). We employ fs transient absorption spectroscopy in the UV/Vis in solution combined with gas phase studies by fs pump-probe fragmentation action spectroscopy [2] to elucidate the underlying ultrafast photophysics and -chemistry as well as the metal-metal-interaction. First results on (1) in dichloromethane with lifetimes $\tau_{1,2,3} = 1.3$, 14.1, 590 ps suggest strongly altered kinetics compared to results on [Ru(bpy)₃]²⁺ [3].

[1] D. M. Knoll et al. Dalton Trans., 2019, DOI: 10.1039/C9DT04366G

[2] D. Imanbaew et al. Angew. Chem. Int. Ed., 2017, 56, 5471-5474
[3] Q. Sun et al. Coord. Chem. Rev., 2015, 282-283, 87-99

MO 8.5 Tue 17:00 Empore Lichthof Ultrafast study of a systematically tuned Ru(II)polypyridine-series in gas phase and solution — •LARS SCHÜSSLER¹, ROUMANY ISRAIL², PATRICK HÜTCHEN², WERNER R. THIEL², CHRISTOPH RIEHN², and ROLF DILLER¹ — ¹Dept. of Physics, TU Kaiserslautern, 67663 Kaiserslautern — ²Dept. of Chem., TU Kaiserslautern, 67663 Kaiserslautern

Ru(II)-polypyridine complexes are widely used in technology and medicine in applications ranging from photovoltaics or catalysis to photoactivatable prodrugs [1]. The respective photoinduced dynamics strongly depend on the relative energies of the ³MLCT- and the ³MC-excited states. Long living phosphorescence competes with photodissociation and -substitution. According to the specific application, a highest possible yield of one of the pathways is desirable and could be controlled by rational ligand design.

Thus, we study a series of the type $[Ru(X-bpy)_2(pyr-na)_2]^{2+}$ (bpy = 2,2'-bipyridine, pyr-na = N-nicotinoyl-pyrrolidine) where X is a varying substituent of different electron withdrawing / donating character to systematically tune the energetics of the ³MLCT- and ³MC-excited states. The photoinduced primary processes are investigated in solution and gas phase by femtosecond transient UV/Vis absorption spectroscopy and pump-probe fragmentation action spectroscopy [2], respectively.

[1] S. E. Greenough et al. PCCP, 2014, 16, 19141-19155

[2] D. Imanbaew et al. Angew. Chem. Int. Ed., 2017, 56, 5471-5474

MO 8.6 Tue 17:00 Empore Lichthof Investigation of the Nitrogen Release Mechanism of a Carbenonitrene Precursor — •NIKLAS GESSNER¹, JULIEN ROWEN², WOLFRAM SANDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Carbenes and the closely related nitrenes are classes of highly reactive molecules. They are commonly generated by photolysis of a diazo or an azido functional group, respectively, releasing molecular nitrogen (N₂). This process is well understood e.g. for the carbene 9-fluorenylidene [1]

MO 8.1 Tue 17:00 Empore Lichthof Multidimensional electronic spectroscopy of a molecular beam with mass-resolved ion detection — •HANS-PETER SOLOWAN, SEBASTIAN ROEDING, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We report on the progress with a new technique, molecular-beam coherent two-dimensional (2D) electronic spectroscopy, enabling multidimensional electronic spectroscopy of gas-phase samples with massresolved ion detection. Using time-of-flight mass spectrometry, we have introduced cations as a new observable in coherent 2D spectroscopy [1]. Using a pulse shaper based on an acousto-optic programmable dispersive filter and rapid scanning [2] we focus a train of four collinear pulses in the visible regime into an interaction region with a molecular beam. Via phase cycling [3] the signals of the time-of-flight mass spectrometer can be disentangled to extract the different contributions, like the photon-echo response. We have recently installed a preparation chamber for a supersonic molecular beam with argon as a seed gas. This allows us to investigate not only gaseous samples but also liquid and solid ones that are evaporated by an oven.

[1] S. Roeding and T. Brixner, Nat. Commun. 9, 2519 (2018)

[2] S. Draeger, S. Roeding, and T. Brixner, Opt. Express 25, 3259 (2017)

[3] H.-S. Tan, J. Chem. Phys. 129, 124501 (2008).

MO 8.2 Tue 17:00 Empore Lichthof Ultrafast photo-ion probing of the ring-opening process in trans-stilbene oxide — •MATTHEW SCOTT ROBINSON, MARIO NIEBUHR, FABIANO LEVAR, DENNIS MAYER, JAN METJE, and MARKUS GÜHR — Universität Potsdam, Institut für Physik und Astronomie, Karl-Liebknecht-Straße 24/25, 14476 Potsdam-Golm, Germany

We study the ultrafast photo-induced ring-opening processes of transstilbene oxide through UV/UV pump-probe time-of-flight experiments with photoion probing and synchrotron-based vacuum ultraviolet ionisation studies, before comparing these results to predictions derived from Woodward-Hoffmann rules.[1]

We fit two major time-dependent features to the parent ion; one sub-90 fs and another of ~260 fs, which match well to theory.[2] We attribute these constants to the primary ring-opening process, likely proceeding via a non-concerted pathway, starting with a sub-90 fs dissociation of the C-C bond in the oxirane ring, followed by the rotation of the phenyl groups to produce the ring-open carbonyl ylide 260 fs after excitation.

We also investigate the appearance of fragment ions, with one in particular (deprotonated diphenylmethane) suggesting an alternative ring-opening pathway not predicted by Woodward-Hoffmann rules, in which dissociation of one of the C-O bonds of the oxirane ring initiates a 1,2-migration of a phenyl group to produce diphenylmethane.

1. Woodward & Hoffmann, Angew. Chemie 81, 797-870 (1969).

2. Friedrichs & Frank, Chem. - A Eur. J. 15, 10825-10829 (2009).

MO 8.3 Tue 17:00 Empore Lichthof Accessing chiral dynamics via broadband time-resolved circular dichroism spectroscopy — •LEA RESS¹, HEIKO HILDENBRAND¹, HOPE BRETSCHER², AKSHAY RAO², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Department of Physics, Cavendish Laboratory, University of Cambridge, 19 JJ Thompson Avenue, Cambridge, United Kingdom

Time-resolved circular dichroism (TRCD) spectroscopy enables the investigation of the ultrafast dynamics of photoinduced chirality changes on a sub-picosecond timescale. We use a pump-probe approach by exciting the sample with a linearly or circularly polarized pump pulse and detecting the difference in absorption of left- and right-circularly polarized probe pulses on a shot-to-shot basis. For this, we developed a setup that is capable of mirroring the polarization state of an ultrashort broadband laser pulse [1].

Here we demonstrate TRCD spectroscopy of monolayer MoS_2 as a proof-of-principle experiment, validating the setup with respect to literature results [2]. In addition to spectroscopy of surfaces, we also investigate the change in chirality of a perylene bisimide folda-dimer or the nitrene 2-fluorenylnitrene [2] that are both long-lived. However, the release mechanism of the carbenonitrene 2-nitreno-9-fluorenylidene (NFl) is still unknown due to the fact that its precursor needs to release in total two molecules of N_2 . This leads to the question whether photochemically, the diazo-nitrene or the azido-carbene is generated first and what happens in subsequent processes.

To address this issue, the generation of NFI in the aprotic solvent acetonitrile has been studied with ultrafast transient absorption spectroscopy. Indications for both a carbene and a nitrene intermediate are found on a picosecond time scale. These transient species can eventually lead to the formation of a carbenonitrene with a quintet ground state, as we identified in separate studies where the compounds are embedded in cryogenic rare-gas matrices.

[1] J. Wang et al., J. Am. Chem. Soc. 129, 13683-13690 (2007).

[2] J. Wang et al., Org. Lett. 25, 5211-5214 (2007).

MO 8.7 Tue 17:00 Empore Lichthof Reaction pathways of a chiral salicylimine studied by ultrafast spectroscopy and vibrational circular dichroism —

•KEVIN ARTMANN¹, CORINA POLLOK², CHRISTIAN MERTEN², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Due to its prominent reaction mechanism and its simple molecular structure, salicylimines were intensively investigated in the past. Upon excitation, an excited-state intramolecular proton transfer (ESIPT) leads to the formation of a keto conformer. In addition, the ESIPT competes with a torsional angle rotation that produces a twisted enol conformer. It has been therefore suggested that the excitation wavelength can influence the population of the different conformers, but there is still no experimental evidence available. In this study, we combine the results from ultrafast transient absorption spectroscopy and matrix-isolation vibrational circular dichroism spectroscopy (MI-VCD) to elucidate the influence of the excitation energy and of the solvent on the reaction mechanism. Besides unraveling the characteristic time scales of the different reaction pathways, it is demonstrated that a higher excitation energy correlates with a lower population of the keto conformer. A higher excitation energy is needed to excite molecules that are already twisted before excitation, therefore the rotational pathway is preferred. Furthermore, we show that the concentration of the keto conformer increases if a solvent with a larger dielectric constant is used.

MO 8.8 Tue 17:00 Empore Lichthof Towards fs UV Measurements of Mass Selective Circular Dichroism in the Gas Phase — •CONSTANTIN WITTE, TOM RING, NICOLAS LADDA, ALEXANDER KASTNER, SIMON RANECKY, SUDHEEN-DRAN VASUDEVAN, HAN-GYEOL LEE, CHRISTIAN SARPE, HENDRIKE BRAUN, ARNE SENFTLEBEN, and THOMAS BAUMERT — Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

The difference in absorption of left and right circularly polarized light is defined as Circular Dichroism (CD). Due to the ubiquity of chirality, its analysis is of great importance. Here, we attempt to measure the CD in the gas phase in the ion yield of chiral showcase molecules camphor and fenchone that have been ionized using a femtosecond laser system. Mass selectivity is achieved via a Time of Flight Mass Spectrometer in Wiley-McLaren Configuration. Generating the third harmonic of our Ti:Sa laser system at 266 nm allows us to reach the $n \to \pi^*$ transition in ketones which promises a high CD according to ns measurements [1]. Generally, a lot of chiral molecules have their absorption bands in the UV. Accessing these with a single photon is beneficial for reaching higher, energetically closer lying states. In the future, this set-up is to be used to investigate and enhance CD effects, determine enantiomeric excess and potentially for enantiomeric purification using coherent control techniques.

[1] Logé, C., Boesl, U.; Multiphoton Ionization and Circular Dichroism: New Experimental Approach and Application to Natural Products, Chem. Phys. Chem. 12, 2011, 1940-1947

MO 8.9 Tue 17:00 Empore Lichthof Photoelectron Circular Dichroism of different monoterpenes and lifetime of their resonances — •SIMON RANECKY, HAN-GYEOL LEE, SUDHEENDRAN VASUDEVAN, ALEXANDER KASTNER, NICOLAS LADDA, TOM RING, CONSTANTIN WITTE, HENDRIKE BRAUN, DANIEL REICH, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany Short lightpulses of 380 nm are able to ionize monoterpenes like fenchone in a resonant 2+1 multi-photon scheme. The ionisation takes place via resonances in the B- and C-Band [1], which can be distinguished by different photoelectron energies. Depending on the pulse length of the laser, the time for relaxation dynamics changes, leading to a different ratio between the photoelectrons from the B- and C-band. By comparison of this pulse length dependence with a quantum-mechanical model system, we estimate the lifetime of the resonances.

The photoelectrons of randomly oriented chiral molecules ionized with circularly polarized light can have an asymmetric momentum distribution in the direction of the laser beam. This effect is called photoelectron circular dichroism (PECD). It can be found in single photon [2], as well as multi-photon ionisation processes with pulse lengths from femtoseconds [1] to nanoseconds [3].

In this study, we examine fenchone, thiofenchone and camphor with pulselengths from femtoseconds to nanoseconds.

- [1] A. Kastner et al., J. Chem. Phys. 147, 013926, (2017)
- [2] L. Nahon et al., J. El. Spectr. 204, 322-334, (2018)
- [3] A. Kastner et al., Chem. Phys. Chem. 20, 1416-1419 (2019)

MO 8.10 Tue 17:00 Empore Lichthof Unraveling the ultrafast dynamics in indole-water — •JOLIJN ONVLEE^{1,2}, JOSS WIESE^{1,3}, JOVANA PETROVIC¹, TERRY MULLINS¹, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3,4} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Center for Ultrafast Imaging, Universität Hamburg — ³Department of Chemistry, Universität Hamburg — ⁴Department of Physics, Universität Hamburg

For a protein in water, hydrogen bonds between the protein and surrounding water molecules strongly affect its folding and thereby also its function. When hydrogen bonds between a protein and surrounding water molecules break, for instance via absorption of UV radiation, the protein structure changes and inactivation of the protein can occur.

We investigated the ultrafast dynamics of the hydrogen-bond breaking between proteins and water in a bottom-up approach by studying the indole molecule – the chromophore of tryptophan, which is the most strongly near-UV absorbing common amino acid – and the indole-water complex, which serves as a model system for the interaction between proteins and water. We produce pure samples of indole and the indole-water complex in the gas phase using a molecular beam and the electrostatic deflector, with which we spatially separate molecular species. The ultrafast dynamics following UV absorption of these molecular species were studied in a pump-probe ion-imaging approach. We also performed laser-induced electron diffraction experiments, with which we aim to record a molecular movie of the hydrogen-bond breaking in indole-water with high spatiotemporal resolution.

MO 8.11 Tue 17:00 Empore Lichthof Photoelectron circular dichroism of chalcogene-substituted fenchone molecules using near UV femtosecond laser pulses — •Sudheendran Vasudevan, Han-gyeol Lee, Tom Ring, Simon Ranecky, Constantin Witte, Nicolas Ladda, Hendrike Braun, Arne Senftleben, and Thomas Baumert — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectron circular dichroism (PECD) is a technique used for sensing molecular chirality with high sensitivity, which arises due to an electric dipole effect [1]. PECD is an asymmetry of the photoelectron emission from a chiral molecule in the forward/backward direction relative to the propagation direction of circularly polarized light field. In this experimental work, we investigate PECD on fenchone molecules where different chalcogene atoms have been substituted in the keto group, e.g. fenchone (oxygen), thiofenchone (sulfur), selenofenchone (selenium). Near ultraviolet laser pulses centred around wavelength of 380 nm, with a pulse duration of around 250 fs and pulse energy of approximately 5 μ J are used to probe these molecules in the gas phase. In the future, a comparative study of the PECD will be done on these molecules by using a wavelength-tunable femtosecond laser source, since PECD is highly dependent on photon energies and energy levels of the molecules [3] which are expected to change by the chemical substitution.

[1] C.Lux et al., Angewandte Chemie 51 (2012): 5001-5005.

[2] C.Lux et al., ChemPhysChem 16 (2015): 115-137.

[3] A.Kastner et al., J. Chem. Phys. 147, 013926 (2017).

MO 8.12 Tue 17:00 Empore Lichthof Frequency-resolved optical gating of low energetic optical pulses — •LARS-STEPHAN KLEIN, LUKAS BRUDER, ULRICH BANGERT, DANIEL UHL, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

We are exploring methods to characterize sub-20 fs pulses with pulse energies $<5 \mathrm{nJ}$. To this end, we investigate the use of second harmonic (SH) frequency-resolved optical gating (FROG), cross-correlation SH FROG and an approach using phase-modulated optical pulses combined with lock-in amplification. The latter is a specialized technique used in two-dimensional electronic spectroscopy (2DES) to improve sensitivity and would allow us to perform pulse characterization directly at the sample position of our 2DES setup. In this context, we also explore the possibility to combine FROG measurements with photoionization.

MO 8.13 Tue 17:00 Empore Lichthof Effect of Chemical Modification and Oxygen Interaction on the Singlet Fission in Azaacene Dimers — •NICOLÒ ALAGNA^{1,2}, JOSE L.P. LUSTRES^{1,2}, SEBASTIAN HAHN³, MARCUS MOTZKUS^{1,2}, UWE H.F. BUNZ³, and TIAGO BUCKUP^{1,2} — ¹Physikalisch Chemisches Institut, Ruprecht-Karls University Heidelberg, Germany — ²Centre for Advanced Materials, University of Heidelberg, Germany — ³Organisch Chemisches Institut, Ruprecht-Karls University, Germany

The solar energy conversion in photovoltaics can be enhanced by singlet fission (SF), a carrier multiplication process where two triplet states T_1 are generated from one absorbed photon. Studies of phenozinothiadiazole derivatives have shown that morphology, packing and chemical structure play a central role in the SF dynamics. Covalently linked dimers can be employed as a model system to selectively study the intramolecular SF. In this work, time-resolved spectroscopy is used to investigate the effect of chemical modification on the intramolecular singlet fission in three directly linked Azaacene-dimers. The analysis of transient absorption and fluorescence dynamics reveals a complex branching mechanism for the singlet (S_1S_0) and the correlated triplet pair $^{1}(TT)$ states. We show that the decay rate and the evolution of the S_1S_0 and $^1(TT)$ states are strongly dependent on the chemical structure. Moreover, the analysis of deaerated solutions reveals the role of oxygen in altering the $^{1}(TT)$ dynamics by introducing new decay pathways.

MO 8.14 Tue 17:00 Empore Lichthof Correlated Electronic Dynamics of Helium in a Chiral Environment — •MANEL MONDELO-MARTELL^{1,2}, CHRISTIANE P. KOCH^{1,2}, and DANIEL M. REICH^{1,2} — ¹Theoretische Physik, Freie Universität Berlin — ²Institut fr Physik, Universität Kassel

Chirality is the fundamental symmetry property defining an object that cannot be superimposed on its mirror image by any translation or rotation. Its relevance in different fields, from AMO physics to drug design, originates in the importance of *chiral interactions*: while both mirror images of a chiral object (enantiomers) will give the same response in front of a non-chiral probe, this is not true when interacting with another chiral system, such as circularly polarized light or aminoacids. This difference allows for chiral discrimination of samples using light, and determines the effects of drugs in our bodies.

In molecular systems, chirality is usually understood in terms of the spacial arrangement of the nuclei. Nevertheless its imprint on the electronic motion, made evident by the Photoelectron Circular Dichroism (PECD) —the asymmetry in forward-backward scattering of the photoelectrons emitted via irradiation with left and right circularly polarized light—, is still not fully understood. Hereby we present timeresolved simulations of the electronic dynamics of the photoionization process of the helium atom in a chiral environment. Through the use of the MCTDHF method[2] we are able to include correlation effects, and give more insight on the role of chirality in the electronic motion.

[1] I. Powis, in Adv. Chem. Phys. (2008), pp. 267-329. [2] J. Zanghellini, et al., Laser Phys. 13, 1064 (2003)

MO 8.15 Tue 17:00 Empore Lichthof **TDCIS Simulations on Chiral Helium** — •MAREC W. HEGER¹, CHRISTIANE P. KOCH², and DANIEL M. REICH^{1,2} — ¹Theoretische Physik, Universität Kassel — ²Institut für Physik, Freie Universität Berlin

Chirality is the property that defines systems that cannot be superimposed on their own mirror image. Current research explores methods for chiral recognition, chiral separation and chiral conversion.

A prominent example for chiral recongnition is the photoelectron circular dichroism (PECD). In PECD experiments a chiral molecule is ionized by left and right circular polarized light and the photoelectron angular distribution then yields a difference for the two polarization directions. Changing the handedness of the chiral molecule inverts the PECD signal which allows for recognition.

Whereas experimental setups for PECD measurements are fairly widespread, theoretical predictions are still sparse. In particular, the simultaneous representation of bound and continuum states for molecular systems, which is necessary for the simulations of time dependent ionization experiments, is still challenging.

Here we present results of the time depentent configuration interaction singles (TDCIS) method performed on a PECD simulation setup. Our approach features a discrete variable representation (DVR) as a numerical basis to represent bound and continuum states and the physical system of interest is helium with an aritficial chiral potential. For helium, full configuration interaction can be performed and consequently we identify the role of electron correlactions for PECD.

MO 8.16 Tue 17:00 Empore Lichthof Exciton Dynamics in Squaraine-based Thin Films — •STEFFEN WOLTER¹, MANUELA SCHIEK², and STEFAN LOCHBRUNNER¹ — ¹Institute of Physics, University of Rostock, 18051 Rostock, Germany — ²Institute of Physics, Carl von Ossietzky University of Oldenburg, 26111 Oldenburg, Germany

Squaraine dyes are promising candidates for light harvesting electron donor materials in small molecule solar cells, since they combine strong absorption in the visible spectral region with a high stability compared to other organic compounds like low bandgap polymers. Bulkheterojunction solar cells based on squaraine:fullerene blends have been shown to suffer from low mobility and recombination losses [1]. In depth understanding of the loss mechanism requires investigation of fundamental processes upon light absorption on ultra-fast time scales.

In this contribution, the light induced processes in different squaraine based thin films are investigated by femtosecond pumpprobe spectroscopy. The dynamics in pure films of 2,4-bis[4-(N,Ndiisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQIB) is studied to obtain a picture of the possible electronic relaxation pathways in the donor material. In a next step, the results are compared to films of SQIB blended with a fullerene acceptor (PCBM). Strong differences in the kinetics and the spectral signatures are observed and attributed to the population of charge separated states.

[1] Scheunemann, Kolloge, Wilken, Mack, Parisi, Schulz, Lützen, Schiek. Appl. Phys. Lett. 111 (2017) 183502.