

MO 15: MO Poster 3

Time: Wednesday 17:00–19:00

Location: Empore Lichthof

MO 15.1 Wed 17:00 Empore Lichthof

Photochemical formation and photophysical properties of photocatalyst radicals — ●SEBASTIAN BERGWINKL and BERNHARD DICK — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany

Recently, organic radicals have been proposed as photocatalysts. Although such radicals are sensitive to oxygen, their electronic excitation leads to potentially strong reducing species that may be used in photoredox catalysis. When these radicals are themselves produced by a photochemical reaction, the catalytic process uses the energy of two photons [1]. Results of time-resolved spectroscopic measurements will be presented that follow the kinetics of the photochemical formation of the rhodamine radical.

Transient absorption spectra obtained with a streak camera show that a single photon absorbed by a rhodamine molecule produces two radicals of this species. One is formed by direct photoinduced electron transfer, the second by a dark reaction on a microsecond time scale, allowing for a theoretical upper limit of the quantum yield of 2. The rhodamine radical is stable for many minutes, but decomposes quickly upon excitation with a second photon.

[1] I. Gosh, T. Gosh, J. I. Bardagi, B. König, *Science* **2014**, 346, 725–728.

MO 15.2 Wed 17:00 Empore Lichthof

Monitoring the photochemistry of a formazan over 12 orders of magnitude in time — ●SVENJA WORTMANN, ROGER JAN KUTTA, and PATRICK NUERNBERGER — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg, Germany

Photoreaction of 2,3,5-triphenyltetrazolium chloride (TTC) in water yields 1,3,5-triphenyltetrazolium formazan (TPF) [1,2], used in TTC assays to indicate cellular respiration or cell growth [3]. From previous studies of formazan analogues only stationary spectra were reported. Exciting at 530 nm, the stable TPF conformer [4] performs an E-Z isomerization to a TPF-stereoisomer, observable by a hypsochromic shift [5]. At least 10 more isomers exist. So far, two conflicting mechanisms are suggested for the light-induced processes in TPF [6].

We studied the photochemistry of TPF in dependence on temperature, excitation wavelength, and solvent environment by time-resolved spectroscopy over 12 orders of magnitude in time. Additionally, vertical excitation energies for each potential TPF conformer were determined by time-dependent density functional theory for assignment of all observed intermediates. Thus, it is shown that the phototriggered dynamics have both ultrafast and very slow contributions with several isomers being accessed along the reaction path.

[1] T. Bolze et al., *ChemPhysChem*, 2018, 19, 138. [2] J. Hausser et al., *Chem. Ber.*, 1949, 82, 195. [3] J. N. Eloff, *Planta Medica*, 1998, 64, 711. [4] F. Kanal et al., *ChemPhysChem*, 2015, 16, 3143. [5] L. S. Atabekyan et al., *High Energy Chem*, 2011, 45, 52. [6] C. Veas-Arancibia, *Diss.*, Louisiana State University, 1986

MO 15.3 Wed 17:00 Empore Lichthof

Temperature and time dependent spectroscopy of tetranuclear d^{10} -complexes with thermochromic emission — ●PATRICK DI MARTINO-FUMO¹, PIT BODEN¹, JASMIN BUSCH², STEFAN BRÄSE², WIM KLOPPER³, and MARKUS GERHARDS¹ — ¹Physical Chemistry, TU Kaiserslautern and State Research Center OPTIMAS, Germany — ²Organic Chemistry, KIT, Germany — ³Physical and Theoretical Chemistry, KIT, Germany

In this contribution a multispectroscopic approach is presented. The combination of spectroscopy with temperature controlled conditions allow the investigation of electronically excited states with respect to structure, energy and lifetimes. The influence of temperature is investigated by a stepwise cooling of the solid samples down to 20 K. The presented molecular systems consist of a series of OLED relevant tetranuclear Cu(I)-complexes in which four Cu(I) centers are bridged by four halides ($X^- = \Gamma, Br^-, Cl^-$) and two *N,P*-units. The main focus is put here on a system with a Cu_4I_4 core and two 6-MePyrPhos ligands, showing an unusual dual emission from two structurally different excited states. The structural changes in the electronically excited states are discussed on the basis of quantum chemical calculations. The emission color is switchable from orange-red to blue by cooling down the sample to 20 K.

MO 15.4 Wed 17:00 Empore Lichthof

Universal Pure Aromatic Hydrocarbon Hosts for High-Efficiency Phosphorescent Organic Light-Emitting Diodes — ●QIANG WANG^{2,3}, FABIEN LUCAS¹, CASSANDRE QUINTON¹, LIANG-SHENG LIAO², ZUO-QUAN JIANG², and CYRIL PORIEL¹ — ¹Univ Rennes, CNRS, ISCR- UMR 6226 35000 Rennes, France — ²Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China. — ³Institut für Physik & IRIS Adlershof Humboldt-Universität zu Berlin 12489 Berlin, Germany

In the field of phosphorescent organic light-emitting diodes (PhOLEDs), heteroatoms are prescriptively used to design host materials with controlled optoelectronic properties. To date, all the very high efficiency universal hosts reported incorporate heteroatoms. However, one of the inherent issues of heteroatom-based hosts is the fragile heteroatom bonds, which causes instability in device performance. Here, we show that pure aromatic hydrocarbons hosts designed with the spirobifluorene scaffold are highly efficient and versatile hosts for PhOLEDs. With external quantum efficiencies of 27.1%, 26.0% and 27.3% for red, green and blue PhOLEDs respectively, this work not only reports the first example of high efficiency pure hydrocarbon host in RGB PhOLEDs but also among the highest performance reported universal host. The overall performance demonstrates that pure aromatic hydrocarbons can provide new perspectives in the design of functional materials for PhOLEDs.

MO 15.5 Wed 17:00 Empore Lichthof

pH-Dependence of Retinal Isomerization in Anabaena Sensory Rhodopsin — ●OSKAR KEFER¹, REI ABE-YOSHIZUMI², HIDEKI KANDORI², and TIAGO BUCKUP¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany — ²OptoBioTechnology Research Center, Nagoya Institute of Technology, Japan

Anabaena sensory rhodopsin (ASR) is a unique microbial retinal protein. In dark adaption the protein contains mostly AT- (all-trans,15-anti) retinal and in photo-equilibrium (light adaptation) a combination of 13C- (13-cis,15-syn) or AT-isomers are present. This enables the investigation of the ultrafast isomerization of these two isomeric chromophores in the same protein environment. pH-Titration experiments in acidic solution have shown two major pKa values (with 4.0 and 6.5) for protonation of residual amino acids, which are involved in the retinal to protein hydrogen-bonding network and influence the steady-state absorption. We use ultrafast transient absorption spectroscopy to investigate the photo-reaction of ASR until the formation of photoproduct "K" under dark and light adaptation. The investigated pH values are chosen to give insight into the effect of the protonation of these amino acids on the isomerization. Our findings indicate a (i) significant acceleration of initial dynamics for AT only for pH 3 and deceleration of "K"-Formation at more acidic solutions and (ii) a monotonic acceleration of the isomerization dynamics of 13C-isomer with increasing pH.

MO 15.6 Wed 17:00 Empore Lichthof

Optical and excitonic properties of molecular aggregates on dielectric surfaces — ●FULU ZHENG, SIDHARTHA NAYAK, and ALEXANDER EISFELD — Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, D-01187 Dresden, Germany

Aggregates of fluorescent dye molecules on dielectric surfaces are of great interest for various technological applications. Due to strong interactions between the molecular transition dipoles, the excitonic eigenstates are coherently delocalized over many molecules [1]. These eigenstates and the corresponding optical transitions are determined by the molecular arrangement. We discuss the dependence of dark and bright states on the molecular arrangement and the spatial shape of the electromagnetic radiation used to probe the aggregate [2]. Strongly inhomogeneous fields can be generated via radiation from the apex of a metallic tip, which allows also scanning across the aggregate. Resulting spatially resolved spectra provide extensive information on the eigenenergies and wave functions [2, 3]. We also found that these delocalized eigenfunctions can be directly reconstructed from spatially resolved near field spectra using convolutional neural networks [3].

[1] A. Eisfeld, C. Marquardt, A. Paulheim, and M. Sokolowski, *Phys. Rev. Lett.* **119**, 097402 (2017). [2] X. Gao and A. Eisfeld, *J. Phys. Chem. Lett.* **9**, 6003 (2018). [3] F. Zheng, X. Gao and A. Eisfeld, *Phys. Rev. Lett.* **123**, 163202 (2019).

MO 15.7 Wed 17:00 Empore Lichthof

Ion-molecule reaction dynamics of atomic oxygen anions with methane — ●ATILAY AYASLI, BJÖRN BASTIAN, TIM MICHAELSEN, JENNIFER MEYER, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Technikerstraße 25/3, 6020 Innsbruck, Austria

We study ion-molecule reactions using a crossed-beam setup with kinematically complete velocity map imaging (VMI) [1]. Currently, we aim to investigate reactive scattering of methane with atomic oxygen anions. The major product channel of the $O^- + CH_4$ reaction forms OH^- via hydrogen abstraction in an exothermic reaction [4]. Energy dependent experiments ranging from 0.34 eV to 0.63 eV collision energy by Carpenter and Farrar [2] revealed two atomistic mechanisms. The major pathway leads to forward scattering at higher collision energies and a significant backward contribution at the lowest collision energy. Recent theoretical studies suggest a minor reaction pathway forming OCH_3^- through an endothermic nucleophilic substitution (S_N2) process at high collision energies [3]. The second pathway has not been previously observed in experiments, as a high entry barrier of 2.54 eV requires higher collision energies. Here, we report on our progress towards $O^- + CH_4$ scattering at higher collision energies to investigate the proposed new reaction pathway.

[1] Wester, *Phys. Chem. Chem. Phys.* **16**, 396 (2014) [2] Carpenter and Farrar, *J. Chem. Phys.* **106**, 5951 (1997) [3] Wang et al., *Molecules*, **23**(10), 2495 (2018) [4] Viggiano et al., *J. Chem. Phys.* **106**, 8455 (1997)

MO 15.8 Wed 17:00 Empore Lichthof

Microsolvation and rotation of *large* molecular impurities inside helium nanodroplets upon electronic excitation — ●MALLIKARJUN KARRA¹, ALEXANDER A. AUER², MIKHAIL LEMESHKO³, GIACOMO BIGHINI³, IGOR CHEREPANOV³, GIOVANNI BISTONI², JOHANNES FISCHER⁴, STEFAN FUCHS⁴, EVA-MARIA LOTTNER⁴, ALKWIN SLENCZKA⁴, and BRETISLAV FRIEDRICH⁴ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Max-Planck-Institut für Kohlenforschung, Mülheim, Germany — ³Institute of Science and Technology Austria, Klosterneuburg, Germany — ⁴Universität Regensburg, Regensburg, Germany

High-resolution electronic spectroscopy (Stark or field-free) of large organic molecules and molecular complexes doped into superfluid helium nanodroplets poses many intriguing questions at the interface of physics and chemistry – especially with regard to solvation and rotation. In our recent work, we have noted the apparent absence of the predicted free rotation of phthalocyanine and porphine in He droplets upon electronic excitation. Extending the study to clusters formed and probed in helium droplets, we also present our surprising finding of a lack of additional helium-stabilized phthalocyanine-water cluster configurations as compared to the gas-phase. We further investigate the absence of a rotational sub-structure in the electronic spectra of dopants larger than glyoxal via a multi-pronged approach that involves the study of the dopant-He PESs before and after electronic excitation, and the invoking of the theory of the angulon quasiparticle in the strong coupling regime.

MO 15.9 Wed 17:00 Empore Lichthof

Quantum chemical studies on chromone/alcohol aggregates - a carbonyl balance for dispersion interactions — ●PATRICK H. STREBERT and MARKUS GERHARDS — Physical Chemistry, TU Kaiserslautern and State Research Center OPTIMAS, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Dispersion forces have often been underestimated in the description of intra- and intermolecular interactions. It is one goal to probe dispersion interactions in dimers with two or more possible binding motifs systematically. In this work, chromone was investigated by quantum chemical methods to examine the binding preference of different aggregating alcohols to the two free electron pairs of the carbonyl group. The balance between dispersion and electrostatic forces can be the deciding factor for the preference of a certain pocket and is difficult to model with current methods. Furthermore, this system is designed to probe weak C-H interactions which further influence the energetic order. Results from different dispersion corrected density functional theory approaches were compared to higher level theory leading to

interesting trends.

MO 15.10 Wed 17:00 Empore Lichthof

Investigating the vibronic structure of photosynthetic pigments using screened range-separated hybrid functionals — ●ALEXANDER SCHUBERT^{1,2,3}, YIN SONG², AKSU HUSEYIN³, JENNIFER P. OGILVIE², EITAN GEVA², and BARRY D. DUNIETZ³ — ¹Friedrich-Schiller Universität Jena, Germany — ²University of Michigan, Ann Arbor, USA — ³Kent State University, USA

Bacteriochlorophyll a (Bchl a) and chlorophyll a (Chl a) play an important role in the initial charge-separation steps in photosynthetic reaction centers. We investigate the interplay of electronic and vibrational states within the Q-band by means of time-dependent density functional theory (TDDFT) employing a recently developed framework based on a screened range-separated hybrid functional within a polarizable continuum model (SRS-PCM). Our simulations support the interpretation of polarized two-dimensional electronic spectroscopic measurements. We find that in Bchl a, the Qx and Qy transitions lead to two independent bands with a relative transition dipole angle of 76° , whereas in Chl a, three distinct peaks of different polarizations are obtained which are traced back to a spectral overlap between two electronic transitions and their vibrational replicas[1]. Furthermore, employing the SRS-PCM scheme to the pseudo-symmetric pigments pairs in bacterial reaction centers reveals that spectral asymmetries may result from locally different effective dielectric environments[2].

[1] *Chem.Sci.*, **10**, p.8143 (2019); [2] *J.Phys.Chem.B.*, **123**(42), p.8970 (2019).

MO 15.11 Wed 17:00 Empore Lichthof

Linearized survival probability for revivals in a Morse oscillator — ●SREEJA LOHO CHOUDHURY and FRANK GROSSMANN — Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

We extend the Husimi (coherent state) based version of linearized semiclassical theories [1] for the calculation of correlation functions to the case of survival probabilities. This is a case that could be dealt with before only by use of the Wigner version of linearized semiclassical theory [2, 3]. Numerical comparisons of the Husimi and the Wigner case with full quantum results as well as with full semiclassical ones will be given for the revival dynamics in a Morse oscillator with and without coupling to an additional harmonic degree of freedom.

[1] S. V. Antipov, Z. Ye, and N. Ananth, *J. Chem. Phys.* **142**, 184102 (2015)

[2] J. Cao and G. A. Voth, *J. Chem. Phys.* **104**, 273 (1996)

[3] E. J. Heller, *J. Chem. Phys.* **65**, 1289 (1976)

MO 15.12 Wed 17:00 Empore Lichthof

A modified approach for simulating nonadiabatic dynamics via the generalized quantum master equation — ELLEN MULVIHILL¹, ●ALEXANDER SCHUBERT^{1,2,3}, XIANG SUN⁴, XING GAO¹, YUDAN LIU¹, BARRY D. DUNIETZ³, and EITAN GEVA¹ — ¹University of Michigan, Ann Arbor, USA — ²Friedrich-Schiller Universität Jena, Germany — ³Kent State University, USA — ⁴New York University Shanghai, China

An approach for simulating nonadiabatic dynamics based on the Nakajima-Zwanzig generalized quantum master equation (GQME) is presented. Unlike the most common GQME-based approaches, the modified approach (M-GQME) does not require casting the overall Hamiltonian in a system-bath form, which is neither natural nor convenient in the case of the molecular Hamiltonian that governs the nonadiabatic dynamics. Within the M-GQME framework, the effect of the degrees of freedom of the environment on the time evolution of the reduced density operator is fully captured by a memory kernel superoperator. Two numerical implementations are presented, where the memory kernel is calculated either employing the Ehrenfest mean-field method [1] or via a combination of the mapping Hamiltonian (MH) approach and the linearized semi-classical (LSC) approximation [2]. Both approaches are demonstrated on a benchmark spin-boson model and shown to lead to significantly more accurate results than a direct application of the Ehrenfest method while being computationally more robust than other GQME-based approaches. [1] *J.Chem.Phys.* **150**, p.034101 (2019). [2] *J.Chem.Phys.* **151**, p.074103 (2019).

MO 15.13 Wed 17:00 Empore Lichthof

A compact UV/VUV spectrometer with fixed VLS gratings for overview luminescence measurements — ●NILS KIEFER, ANDREAS HANS, ARNO EHRESMANN, and ANDRÉ KNIE — Insti-

tut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSA-T), Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

We present a design study for the energy resolved photon detection in the UV and XUV energy regime. A grating with Variable Line Spacing (VLS) allows for dispersion of a wide spectral range onto flat detector surfaces. With two VLS gratings on one substrate, spectra from 30nm to 120nm and 120nm to 300nm can be imaged simultaneously, but spatially separated. In order to achieve single photon detection, two position and time resolving MCP-based detectors will be used. Exemplary showcase-applications at FAIR (Facility of Antiproton and Ion Research) and synchrotron radiation facilities will be outlined. With this compact spectrometer with high efficiency and high resolution from 30nm to 300nm, it will be possible to collect time efficiently wide range luminescence spectra in experiments for the characterization of the highly charged ion beams or synchrotron radiation served AMO experiments.

MO 15.14 Wed 17:00 Empore Lichthof
Chirped-Pulse Microwave Spectroscopy of Complex Molecules — •BETTINA HEYNE¹, MARIUS HERMANN¹, NADINE WEHRES¹, CHRISTIAN ENDRES², and STEPHAN SCHLEMMER¹ — ¹First Physics Institute, University of Cologne, Germany — ²Max Planck Institute for Extraterrestrial Physics, Garching, Germany

The Cologne chirped-pulse microwave spectrometer for molecules relevant for astrophysics is operational between 12 and 26.5 GHz and has been described before [1]. Here, the basic principle and the experimental setup will be presented [2]. First, noise measurements taken with the hot-cold method will be discussed. Furthermore, the sensitivity was determined by using a spectrum of OCS and its different isotopologs. Moreover, a closer examination of OCS at different temperatures will be shown and an intensity calibration will be performed. In addition, a spectrum of 2-cyanobutane recorded with a heatable nozzle will be presented.

References: [1] M. Hermanns, N. Wehres, F. Lewen, H.S.P. Müller, S. Schlemmer, *Journal of Molecular Spectroscopy*, 358, 25-36 (2019)

[2] B. Heyne, Master Thesis 'Chirped-Pulse Fourier Transform Spectroscopy of Complex Molecules' (2019)

MO 15.15 Wed 17:00 Empore Lichthof
Emission spectroscopy using heterodyne receivers — •NADINE WEHRES, BETTINA HEYNE, MARIUS HERMANN, JAKOB MASSEN, KIRILL BORISOV, KATHARINA VON SCHOELER, PATRICK PÜTZ, CORNELIA NONINGH, URS GRAF, FRANK LEWEN, and STEPHAN SCHLEMMER — I. Physics Institute, University of Cologne, Cologne, Germany

Two laboratory emission spectrometers between 70-110 GHz (coincident with ALMA Band 3) and 300-400 GHz (coincident with ALMA Band 7) have been described before [1,2] and will be discussed here with special focus on its stability and sensitivity, as well as its prospects on absolute intensity calibration [3]. Following-up on these recent advances towards heterodyne detection, we present preliminary results using the SOFIA (Stratospheric Observatory for IR Astronomy) up-GREAT laboratory setup, operational around 2 THz, for the spectroscopy of complex molecules. First spectra focus on pure rotational transitions of vinyl cyanide (C₂H₃CN). These spectra are used to estimate intensities of ro-vibrational transitions coming from low-lying vibrational bands of polycyclic aromatic hydrocarbons (PAHs). The

results are used as feasibility study to exploit future research directions for the spectroscopy of the fingerprint-like ro-vibrational transitions of PAHs at around 2 THz.

References:

[1] N. Wehres, et al. *IAUS* 332 (2018)

[2] N. Wehres, et al. *PCCP* 20, 5530 (2018)

[3] N. Wehres, et al. *IAUS* 350 (2019, accepted)

MO 15.16 Wed 17:00 Empore Lichthof
Novel sample delivery system for small nanoparticles and biomolecules — •LENA WORBS^{1,2}, JANNIK LÜBKE^{1,2,3}, ARMANDO ESTILLORE¹, AMIT K. SAMANTA¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Fachbereich Physik, Universität Hamburg — ³Center for Ultrafast Imaging, Hamburg

Coherent diffractive imaging with free-electron lasers promises to allow the reconstruction of the three-dimensional molecular structures of isolated particles at atomic resolution [1]. However, because of the typically low signal-to-noise ratio, this requires the collection of a large amount of diffraction patterns. Since every intercepted particle is destroyed by the intense x-ray pulse, a new and preferably identical sample particle has to be delivered into every pulse.

We present a novel injection scheme, combining electrospray ionization for aerosolization of the sample, followed by shock-freezing and focusing techniques to produce a collimated or focused nanoparticle beams of a broad variety of biological nanoparticles, ranging from large nanoparticles to small single-domain proteins. These nanoparticle beams can be further manipulated to separate, for instance, charge states or conformational states, to allow pure samples to be delivered into the x-ray focus.

[1] M. M. Seibert, et al, *Nature* **470**, 78 (2011).

MO 15.17 Wed 17:00 Empore Lichthof
Efficient Ytterbium Near-Infrared Luminophore Based on a Nondeuterated Ligand — •PARIYA NAZARI¹, CHRISTIAN KRUCK², CAROLIN DEE², MICHAEL SEITZ², IAN HOWARD^{1,3}, BRYCE S. RICHARDS^{1,3}, and ANDREY TURSHATOV¹ — ¹Institute of Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT) — ²Institute of Inorganic Chemistry, University of Tübingen — ³Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT)

Near-infrared lanthanoid(III) luminophores are highly interesting for technological applications such as biomedical imaging, and spectral conversion materials. The main challenge for the development of efficient, molecular, near-IR emitter complexes is the vibrational deactivation of metal-centered states by multiphonon relaxation where the energy is transferred from the lanthanoid to high-energy oscillators such as O-H and C-H in its vicinity. The two main strategies to alleviate the problem in the ligands are removing these oscillators by either deuteration or halogenation. While the development of deuterated/halogenated near-IR ytterbium luminophores has made great progress, there is still a need for molecular emitters that are relatively simple to prepare, yet still able to exhibit acceptable luminescence efficiency. In this study, we comprehensively characterize the photophysics of a novel molecular ytterbium complex with a new tetradentate ligand based on the 2,2-bipyridine-6,6-dicarboxylic acid scaffold. The ytterbium complex shows a rather high absolute luminescence quantum yield of 3.0% and a luminescence lifetime of 72 μ s at room temperature in deuterated-methanol solution.