

## MO 18: Posters 2: Time Resolved Spectroscopy

Time: Wednesday 16:15–18:15

Location: S Foyer LLM

MO 18.1 Wed 16:15 S Foyer LLM

**Time-Resolved step-scan FTIR investigations of luminescent first row transition metal complexes** — ●PIT BODEN<sup>1</sup>, PATRICK DI MARTINO-FUMO<sup>1</sup>, SVEN OTTO<sup>2</sup>, MATTHIAS DORN<sup>2</sup>, CLAUDIA BIZZARRI<sup>3</sup>, KATJA HEINZE<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry, TU Kaiserslautern, Germany — <sup>2</sup>Inorganic Chemistry and Analytical Chemistry, JGU Mainz, Germany — <sup>3</sup>Organic Chemistry, KIT, Germany

In this contribution, the time-resolved step-scan FTIR technique is used for investigations of highly luminescent first row transition metal complexes in their electronically excited states with lifetimes in the microsecond regime. The vibrational frequencies obtained from this technique, compared with theoretical calculations, allow for a structural assignment of the excited states. The chosen molecular systems include a series of mononuclear Cr<sup>3+</sup>-complexes with dipyrindium ligands. These NIR-emitting complexes have a very high luminescence quantum yield and two energetically close lying doublet states, where the relative population can be influenced by cooling down a solid sample to at least 20 K or by applying the newly developed double resonance techniques. The analysis is extended to a related V<sup>3+</sup>-complex. Additionally, a photosensitive mononuclear Cu(I)-complex and its bridged binuclear analogue are investigated. By comparison with theoretical results, the structures of the electronic ground and lowest lying electronically excited state are determined.

MO 18.2 Wed 16:15 S Foyer LLM

**Photodynamics of an Iron-based Photosensitizer after Deep-UV Excitation** — ●NIKLAS GESSNER<sup>1</sup>, LION-LUCA STIEWE<sup>1</sup>, JOHANNES MOLL<sup>2</sup>, KATJA HEINZE<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44801 Bochum — <sup>2</sup>Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz

Photosensitizers are capable of transferring their energy to adjacent molecules after photoexcitation. However, many compounds used in this way in medicine or photovoltaics are complexes of rare noble metals. In contrast to this, [Fe(cpmp)<sub>2</sub>]<sup>2+</sup> comprises an earth-abundant central iron atom that may significantly reduce costs.

In this contribution, we study its photochemical properties with transient absorption spectroscopy in the ultraviolet, visible and mid-infrared (MIR) after excitation at 280 nm to a highly energetic state. Initially, [Fe(cpmp)<sub>2</sub>]<sup>2+</sup> exhibits dynamics on a timescale of 10 ps associated with vibrational cooling and rapid relaxation to a long-lived excited state which shows an excited-state absorption (ESA) around 320 nm. Subsequently, this ESA, the MIR signatures as well as the ground-state bleach decay with the same untypically short time constant of ≈540 ps. In accordance with related compounds [1,2], the study discloses that [Fe(cpmp)<sub>2</sub>]<sup>2+</sup> belongs to the recently emerging class of iron(II) compounds with a strong ligand field so that the system reaches a long-lived <sup>3</sup>MC (metal centered) state.

[1] L. L. Jamula *et al.*, *Inorg. Chem.* **53**, 15-17 (2014).[2] A. K. C. Mengel *et al.*, *Chem. Eur. J.* **21**, 704-714 (2015).

MO 18.3 Wed 16:15 S Foyer LLM

**Spin-flip dynamics in transition metal complexes triggered by soft X-ray light** — ●VLADISLAV KOCHETOV, HUIHUI WANG, and SERGEI BOKAREV — Institut für Physik, Universität Rostock, 18059 Rostock

The prominent development of intense X-ray laser technologies stimulates theoretical studies of phenomena occurring at ultra-short timescales. Time-resolved experiments revealing the energy and charge transfer effects in molecular systems are of great importance. Here we present the investigation of spin-flip dynamics of an iron complex triggered by short X-ray pulses. The process of core excitation and consecutive changes in spin populations are simulated and analyzed in terms of density matrix within the time-dependent restricted active space configuration interaction theory. Calculations take into account the nuclear motion as a vibrational bath and Auger decay via quantum master equation in the Markov approximation. The detailed analysis of spin population distributions evolving during the first femtoseconds after excitation is presented and the role of electron correlation in the spin-flip process is discussed in the current work. Also, the influence of different ligands and various pulse characteristics on the initiated dy-

namics is demonstrated suggesting the design of possible experiments and applications in spintronics.

MO 18.4 Wed 16:15 S Foyer LLM

**Cooperative effects in Ir, Pt and Pd containing bimetallic complexes** — ●TATJANA WALL<sup>1</sup>, MARKO LEIST<sup>2</sup>, WERNER R. THIEL<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> — <sup>1</sup>Physical Chemistry, TU Kaiserslautern — <sup>2</sup>Inorganic Chemistry, TU Kaiserslautern

Bimetallic complexes can show cooperative effects between the metal centers that can influence spectroscopic properties as well as their performance in catalysis. To investigate such effects, absorption and emission spectra of a homologous series of mono- and binuclear transition metal complexes based on (2-dimethylamino)-4-(2-pyrimidinyl)pyrimidine in different solvents were recorded. Furthermore the lifetimes of the excited states were determined by using the time correlated single photon counting (TCSPC) method. Here we represent the results for Ir, Pt and Pd containing complexes. The results are compared with the pure ligand and additionally a comparison with DFT calculations is performed. For both types of complexes, mono- as well as binuclear ones, MLCT (Metal to Ligand Charge Transfer) and ligand centered bands are observed. The shifts of these bands compared to the pure ligand give information about cooperative effects. Lifetime determinations show multiple exponential decays for both emission bands, whereas the pure ligand has a mono-exponential decay. The photophysics of complexes with respect to lifetimes, coordinations and characters of electronically excited states are discussed.

MO 18.5 Wed 16:15 S Foyer LLM

**Mapping of exciton-exciton annihilation in a molecular dimer via fifth-order femtosecond two-dimensional spectroscopy** — ●JASMIN SÜSS<sup>1</sup>, JOHANNES WEHNER<sup>1</sup>, JAKUB DOSTÁL<sup>2,3</sup>, TOBIAS BRIXNER<sup>2,3</sup>, and VOLKER ENGEL<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Am Hubland, 97074 Würzburg, Germany — <sup>3</sup>Center for Nanosystems Chemistry (CNC), Theodor-Boveri-Weg, 97074 Würzburg, Germany

We present a theoretical study on exciton-exciton annihilation (EEA) in a molecular dimer. This process is monitored using a fifth-order coherent two-dimensional (2D) spectroscopy as was recently proposed by Dostál *et al.* (*Nat. Commun.* **9**, 2466 (2018)). Using an electronic three-level system for each monomer, we analyze the different paths which contribute to the two-dimensional spectrum. The spectrum is determined by two entangled relaxation processes, namely the EEA and the direct relaxation of higher lying excited states. It is shown that the change of the spectrum as a function of a pulse delay can be linked directly to the presence of the EEA process.

MO 18.6 Wed 16:15 S Foyer LLM

**Exciton Dynamics of Carbocyanine J-Aggregates in Polymer Films** — ●STEFFEN WOLTER<sup>1</sup>, ALEXANDER V. SOROKIN<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, 18051 Rostock, Germany — <sup>2</sup>Institute for Scintillation Materials of NAS of Ukraine, SSI Institute for Single Crystals of NAS of Ukraine, 60 Nauky ave., 61072 Kharkiv, Ukraine

J-aggregates are promising candidates as building blocks for future photonic applications. These supramolecular structures typically feature high quantum yields and exciton mobilities at ambient conditions, although the actual values highly depend on the local environment. J-aggregates in thin polymer films are of particular interest for applications. However, most studies deal with aggregates in solution and the behavior of the aggregates in polymers is insufficiently characterized. In this contribution, the influence of different local environments on the exciton dynamics is investigated by femtosecond pump probe spectroscopy for J-aggregates consisting of the carbocyanine dye 1,1'-disulfobutyl-3,3'-diethyl-5,5',6,6'-tetrachlorobenzimidazolylcarbo-cyanine sodium salt (TDBC). The dye forms J-aggregates in polymer films with optical properties comparable to those in water solutions, however, with a much lower fluorescence quantum yield. The goal is to understand this finding and to learn about the responsible mechanism.

MO 18.7 Wed 16:15 S Foyer LLM

**THz Spectroscopy on Charge Carriers in Organic Semiconductors** — ●PHILIPP KRAUSPE, JULIEN RÉHAULT, MARTINA CAUSA<sup>1</sup>, DEMETRA TSOKKOU, and NATALIE BANERJI — Universität Bern, Freiestrasse 3, 3012 Bern

In this work we present optical pump - THz probe (OPTP) studies on organic semiconductors. [1] These semiconductors are polymer:fullerene blends which are used for organic photovoltaics. Our THz spectroscopy reveals the time evolution of charge carriers and their relative mobility on short distances. By changing the material system and selectively exciting the compounds we isolate separate pathways from photoexcitation to free carrier that transports the solar energy to the outer contacts. We present these findings in combination with transient absorption and electro differential absorption measurements on the same material systems.

Furthermore, we introduce a novel spectroscopic technique aiming at the first few picoseconds revealing the charge generation process upon photoexcitation. In this THz emission spectroscopy we generate a THz waveform within an active layer by applying a constant bias that accelerates the free charges.

[1] P. Krauspe, D. Tsokkou, M. Causa\*, E. Buchaca-Domingo, Z. Fei, M. Heeney, N. Stingelin, N. Banerji: Terahertz Short-Range Mobilities in Neat and Intermixed Regions of Polymer: Fullerene Blends with Controlled Phase Morphology. *Journal of Materials Chemistry A* (2018)

MO 18.8 Wed 16:15 S Foyer LLM

**Effect of External Electric Field on Charge-Pair Dynamics in Poly-[3-Hexylthiophene] (P3HT): A Femtosecond Time-Resolved Study** — ●DEBKUMAR RANA, PATRICE DONFACK, VLADISLAV JOVANOVIĆ, VEIT WAGNER, and ARNULF MATERNY — Jacobs University Bremen, Department of Physics & Earth Sciences, Campus Ring 1, 28759, Bremen, Germany

Organic semiconductors have attracted considerable attention in recent years. However, a complete fundamental understanding of the relevant elementary processes is still missing. Several subtle processes such as those involving bound states (*e.g.* charge-pair states) are crucial to the overall macroscopic picture of device performance based on free charge carriers. In our contribution, we have investigated the dynamics of charge-pair states in Poly-[3-hexylthiophene] (P3HT), a promising organic semiconductor already studied by many researchers, utilizing standard and electric field-dependent transient absorption spectroscopy in order to obtain a realistic picture of the dynamics, since typical devices operate under an applied voltage in practice.

We have found that due to dissociation in the presence of external electric fields, charge-pair recombination time scales and pathways are significantly affected. Especially, our study has revealed a direct observation of different kinds of charge pairs as the result of an applied reverse bias, which we have attributed to typical polaron pairs and loosely bound polaron pairs. These charge pairs have shown completely different dynamics in our study. We will present and discuss our first experimental results.

MO 18.9 Wed 16:15 S Foyer LLM

**Ultrafast Electronic Dynamics and Optical Excitation of Phonons in Hafnium Disulfide Crystals** — ●SIMON UNGER<sup>1</sup>, FRANZISKA FENNEL<sup>1</sup>, CHRIS REHHAGEN<sup>1</sup>, TIM VÖLZER<sup>1</sup>, KAI ROSSNAGEL<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute for Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock — <sup>2</sup>Institute for Experimental and Applied Physics, University of Kiel, Leibnizstr. 19, 24118 Kiel

Transition metal dichalcogenides feature unique electronic and optical properties. Additionally, they consist of a layered structure, allowing the preparation of atomically thin crystals. Hafnium disulfide, as a representative of those materials, is considered to be a promising candidate for electronic and optoelectronic applications. To investigate the internal electronic processes and decay dynamics, static absorption and femtosecond pump-probe measurements were performed.

In the absorption spectrum, two bands are observed in the UV range. In the femtosecond pump-probe experiments, the sample is excited in the range of those bands and probed by a following white light pulse. The transient absorption signal shows a strong reduction in absorbance in the region of the original absorption, whereas at longer wavelengths a signal increase appears. This feature is an indication for a band gap renormalization induced by the population of excited charge carriers. The temporal evolution exhibits a fast sub-picosecond and a slower sub-nanosecond decay, caused by the relaxation and recombination of the charge carriers. Furthermore, the time traces show an oscillation

pattern, which can be attributed to the excitation of acoustic phonons.

MO 18.10 Wed 16:15 S Foyer LLM

**Porphyrim-functionalized covalent organic cage compounds as prototypical artificial light-harvesting systems** — ●LYSANNE MONIKA DIETRICH<sup>1,2</sup>, MATTHIAS HENSEN<sup>1</sup>, EVGENII TITOV<sup>1</sup>, ROLAND MITRIC<sup>1</sup>, FLORIAN BEUERLE<sup>2</sup>, and TOBIAS BRIKNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Institut für Organische Chemie & Zentrum für Nanosystemchemie, Universität Würzburg, Am Hubland, 97074 Würzburg

One key challenge for the future will be to learn how to construct artificial molecular devices enabling the harvesting of sunlight and their use for photosynthetic approaches. Recent studies suggested that the flexibility of the donor-acceptor linking group of artificial photosynthetic materials is an important parameter for optimizing their performance [1]. In order to improve the understanding of photoinduced electron transfer processes characteristic of photosynthesis, we designed a novel porphyrin-containing covalent organic cage compound that can serve as an efficient host for [60]fullerene. Upon photoexcitation of the porphyrin donor moiety, an electron transfer to the encapsulated [60]fullerene is triggered presumably on the ultrafast timescale. Here we report on investigations on electron transfer processes of these supramolecular porphyrin fullerene hybrid systems by means of femtosecond transient absorption spectroscopy and quantum chemical calculations.

[1] C. A. Rozzi et. al., *Nat. Commun.* 4, 1602 (2013).

MO 18.11 Wed 16:15 S Foyer LLM

**Transient Absorption Spectroscopy of Photo-induced Guest Uptake and Release by a Photochromic Coordination Cage** — ●KEVIN ARTMANN<sup>1</sup>, RUJIN LI<sup>2</sup>, DOMINIK WELZEL<sup>1</sup>, GUIDO H. CLEVER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — <sup>2</sup>Anorganische Chemie, Technische Universität Dortmund, 44227 Dortmund

Encapsulation of guest compounds by molecular cages are a promising tool in a variety of applications. It can be used to protect, to transport, or to influence the reactivity of guest molecules, but also *vice versa* the guest may modify the properties of the host. Recently, Han *et al.* demonstrated that it is possible to trigger the reversible guest encapsulation with light by using cage systems composed of photo-switchable dithienylethene ligands [1].

In this study we investigate the influence of a guest compound on the ultrafast photodynamics of these cages. We demonstrate that the dynamics of the single ligand and of the cage in solution are similar to those of a closely related derivative examined by Ern *et al.* [2]. Furthermore, we show that the photodynamics of the cage with ring-closed ligands do not change after addition of the guest. In contrast, encapsulation of the guest in cages with ring-open ligands reduces the efficiency of the ring-closing reaction and gives rise to the population of another intermediate state.

[1] Han *et al.*, *Angew. Chem. Int. Ed.* 52, 1319-1323 (2013).

[2] Ern *et al.*, *J. Phys. Chem. A* 105, 1741-1749 (2001).

MO 18.12 Wed 16:15 S Foyer LLM

**Excited State Dynamics of the Amino Acid Tryptophan** — ●PASCAL ENGL, JANINA LEBENDIG-KUHLA, and ANDREA LÜBCKE — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin

The amino acid tryptophan is known to be involved in ultra-fast processes like energy and electron transfers in proteins. We investigate the excited state dynamics of tryptophan in solution and its chromophore indole in the gas phase by utilizing pump-probe time-resolved photoelectron spectroscopy (TRPES). This method allows us to follow photoreactions in both energy and time by mapping the molecule's excited state dynamics onto the continuum. As pump and probe pulses we use fs UV-laser pulses with wavelengths of 200 nm and 266 nm. For the measurements in aqueous solution we employ the liquid microjet technique. We will describe our experimental setup, present our results and discuss the effects of the environment on the excited state dynamics.

MO 18.13 Wed 16:15 S Foyer LLM

**Quick Photoshoot: time-resolved imaging of the azobenzene isomerization with ultra-fast electron diffraction** — ●MARIO NIEBUHR<sup>1</sup>, KEITH JOBE<sup>2</sup>, RENKAI LI<sup>2</sup>, J. PEDRO F. NUNES<sup>4</sup>, XIAOZHE SHEN<sup>2</sup>, STEPHEN WEATHERSBY<sup>2</sup>, THOMAS J. A. WOLF<sup>3</sup>,

CHARLES YONEDA<sup>2</sup>, JIE YANG<sup>2,3</sup>, MARTIN CENTURION<sup>4</sup>, XIJIE WANG<sup>2</sup>, and MARKUS GÜHR<sup>1</sup> — <sup>1</sup>Institute for Physics and Astronomy, Uni Potsdam, Germany — <sup>2</sup>SLAC National Accelerator Laboratory, USA — <sup>3</sup>PULSE Institute, SLAC National Accelerator Laboratory, USA — <sup>4</sup>Department of Physics & Astronomy, University of Nebraska-Lincoln, USA

The processes involved in the trans-cis isomerization of azobenzene are still actively discussed. One issue in question are different proposed relaxation pathways after Vis or UV excitation, resulting in distinct intermediate geometries. While calculations generally suggest the so called inversion pathway, to our knowledge no direct observation has been performed confirming one or the other.

Photon pump electron probe diffraction experiments on isolated molecules in the gas phase promise to allow just that. New ultrafast electron diffraction setups with MeV beams offer a new approach to that question [1] mitigating the disadvantages of current keV systems (velocity mismatch, electron beam divergence) and allowing for sub-100 fs time resolution to observe the azobenzene reconfiguration during the trans-cis isomerization. We will show results from our first run with the UED group at SLAC and discuss planned improvements.

[1] Weathersby et al., Rev. Sci. Instrum. **86**, 073702 (2015)

MO 18.14 Wed 16:15 S Foyer LLM

**Charge transfer in mixed valence states: Relaxation dynamics and transient absorption spectroscopy** — ●FABIAN GLAAB<sup>1</sup>, JOHANNES WEHNER<sup>1</sup>, CHRISTOPH LAMBERT<sup>2</sup>, and VOLKER ENGEL<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Quantum dynamical model calculations are performed on the laser-induced dynamics of mixed valence systems. The simultaneously occurring processes of non-adiabatic population transfer and relaxation are studied in detail. Transient absorption traces, as recently recorded in our laboratory [1], are simulated, and the features of the spectra are related to the dynamics. The agreement with experiment hint at the fact that the employed one-dimensional model catches the essentials of the photochemistry of the mixed valence systems under consideration.

[1] C. Lambert, M. Moos, A. Schmiedel, M. Holzappel, J. Schäfer, M. Kess, V. Engel, V., Phys. Chem. Chem. Phys. **18**, 19405-19411 (2016).

MO 18.15 Wed 16:15 S Foyer LLM

**Multidimensional electronic spectroscopy of a molecular beam with mass-resolved ion detection** — ●HANS-PETER SOLOWAN, TRISTAN FORD, SEBASTIAN ROEDING, and TOBIAS BRIXNER — 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 mass-resolved 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 18.16 Wed 16:15 S Foyer LLM

**Ultrafast 2D-Vis spectroelectrochemistry** — ●JULIA HEITMÜLLER, KLAUS ECKSTEIN, PASCAL KUNKEL, TOBIAS BRIXNER, and TOBIAS HERTEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent 2D spectroscopy is a well established method to investigate dynamic processes with femtosecond time resolution and to observe

couplings between different energetic states. Electrochemistry is used to generate different oxidized and reduced molecular species in solution. Our goal is the combination of these two techniques leading to coherent 2D spectroelectrochemistry. For the infrared regime different spectroelectrochemical cells were described and used for 2D measurements in the literature [1,2]. We developed a prototype for the visible regime to investigate UV/Vis-induced photophysics or photochemical reactions depending on oxidation state. We verified that our design works, by using redox standards and laser dyes. First time-resolved measurements were performed by integrating the cell in transient absorption experiments. In the next step we will approach 2D spectroscopy and observe molecules in different redox states, that are generated *in situ* without adding oxidizing or reducing agents.

[1] Y. El Khoury, et al., Rev. Sci. Instrum. **86**, 083102 (2015)

[2] D. Lotti, et al., J. Phys. Chem. C, **120**, 2883 (2016)

MO 18.17 Wed 16:15 S Foyer LLM

**Ultrafast Photoelectron Circular Dichroism Changes in 1-Iodo-2-methylbutane** — ●V. MUSIC<sup>1,2</sup>, F. ALLUM<sup>4</sup>, S. BARI<sup>3</sup>, T. M. BAUMANN<sup>1</sup>, R. BOLL<sup>1</sup>, S. DOERNER<sup>3</sup>, A. EHRESMANN<sup>2</sup>, B. ERK<sup>3</sup>, P. GRZYCHTOL<sup>1</sup>, G. HARTMANN<sup>2</sup>, A. KNIE<sup>2</sup>, M. LARSSON<sup>7</sup>, J. LEE<sup>4</sup>, B. MANSCHWETUS<sup>3</sup>, L. MARDER<sup>2</sup>, R. MASON<sup>4</sup>, M. MEYER<sup>1</sup>, H. OTTO<sup>2</sup>, D. ROLLES<sup>5</sup>, P. SCHMIDT<sup>2</sup>, K. SCHUBERT<sup>3</sup>, L. SCHWOB<sup>3</sup>, R. WAGNER<sup>1</sup>, V. ZHAUNERCHYK<sup>6</sup>, and M. ILCHEN<sup>1,2</sup> — <sup>1</sup>European XFEL GmbH, Schenefeld, Germany — <sup>2</sup>University of Kassel, Germany — <sup>3</sup>DESY, Hamburg, Germany — <sup>4</sup>University of Oxford, UK — <sup>5</sup>Kansas State University, Manhattan, USA — <sup>6</sup>University of Gothenburg, Sweden — <sup>7</sup>AlbaNova University Center, Stockholm, Sweden.

Highly intense circularly polarized XUV free-electron laser pulses were used to observe the time-resolved photoelectron circular dichroism (TR-PECD) of a prototypical chiral molecule as 1-Iodo-2-methylbutane ( $C_5H_{11}I$ ) during laser induced fragmentation. The presented experiment was performed at the BL1 CAMP endstation at FLASH1 in Hamburg. With a two-sided velocity map imaging spectrometer, electron-ion correlations were obtained and the time-resolved ejection of ionic and neutral atomic iodine was observed. These fragments serve as observer site to monitor the evolving chirality of the molecule. For probing the different fragmentation channels of the chiral molecule (R-enantiomer, S-enantiomer and the racemic mixture), two different photon energies, i.e. 63 eV (for neutral iodine) and 75 eV (for singly charged iodine), were used.

MO 18.18 Wed 16:15 S Foyer LLM

**Theoretical interpretation of angular-resolved photoelectron pump-probe spectroscopy** — ●ANDY KAISER, SERGEY BOKAREV, and OLIVER KÜHN — Institute of Physics, Rostock, Germany

Photoelectron spectroscopy is a powerful probe of the electronic structure of atoms and molecules. Orbital structure, energy levels and non-adiabatic dynamics can be analyzed within pump-probe experiments. Varying the time delay between the pulses gives information about wave packet dynamics and potential energy surfaces. This knowledge allows to optimize chemical processes and learn about spin crossover phenomena. In this work randomly oriented transition metal complexes were studied theoretically in the solution phase. First, molecules are preselected by a short pump-pulse. After a short time delay, which lies in fs range such that translational and rotational degrees of freedom can be considered as frozen, the sample interacts with the probe pulse, ejecting a photoelectron, which is then resolved angularly giving information about the electronic structure. The working expression in this simulation is the photoelectron matrix element formulated in the Dyson orbital formalism and the outgoing photoelectron described by Coulomb waves. To obtain accurate energies of both, the system and the photoelectron, optimally-tuned, range-separated density functionals were used within TDDFT.

MO 18.19 Wed 16:15 S Foyer LLM

**Pulse Length Dependence of Photoelectron Circular Dichroism** — ROXANA SAVULEA, ●SIMON T. RANECKY, CONSTANTIN WITTE, ALEXANDER KASTNER, TOM RING, HAN-GYEOL LEE, SUDHEENDRAN VASUDEVAN, HENDRIKE BRAUN, DANIEL REICH, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSA/T, D-34132 Kassel, Germany

The asymmetry of photoelectron angular distributions from randomly oriented enantiomers of chiral molecules in the ionization with circularly polarized light arises in forward/backward direction with respect to the light propagation direction. This effect is known as photoelec-

tron circular dichroism (PECD) and has been investigated by single-photon [1] as well as resonance-enhanced multi-photon ionization using a femtosecond laser [2, 3]. In that case, ionization occurs out a frozen nuclear configuration. For longer pulses, additional dynamics like internal conversion, intra-molecular vibrational energy redistribution, vibrations or rotation of the molecules come into play.

Here we present a coherent pulse length study to investigate PECD ranging from the femtosecond to the nanosecond regime. To that end, we employ a femtosecond laser with variable pulse duration and a nanosecond dye laser. When using the latter, the lifetime of the intermediate states is much shorter than the pulse duration of the laser.

[1] L. Nahon et al., *J. El. Spectr.* 204, 322-334, (2015)

[2] C. Lux et al., *Chem. Phys. Chem.* 16, 115-137, (2015)

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

MO 18.20 Wed 16:15 S Foyer LLM

**Role of coherence for photoelectron circular dichroism after multi-photon excitation in randomly oriented chiral molecules** — ●ALEXANDER BLECH<sup>1</sup>, R. ESTEBAN GOETZ<sup>1</sup>, TIMUR A. ISAEV<sup>2</sup>, BEHNAM NIKOBAKHT<sup>2</sup>, ROBERT BERGER<sup>2</sup>, and CHRIS-

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Photoelectron circular dichroism (PECD) refers to the forward/backward asymmetry in the photoelectron angular distribution with respect to the propagation axis of circularly polarized light. Our existing model for PECD in resonantly enhanced multi-photon ionization of randomly oriented chiral molecules is based on perturbation theory for the light-matter interaction and on ab initio calculations for the multi-photon absorption, giving semi-quantitative agreement with experimental data for fenchone and camphor and enabling application of coherent control.

Here we want to extend this model to explicitly take into account the chirality of the photoelectron continuum and the coherence between non-resonant multi-photon excitation and one-photon ionisation by standard quantum beat spectroscopy of electronic superposition states in a pump-probe scheme. Our extended model will allow us to distinguish the contributions of intermediate and final states to PECD and to refine our quantum optimal control approach in order to determine the ultimate strength of the chiral response.