O 88: Focus Session: Ultrafast Processes in Organic Semiconductors and Perovskites II (joint session O/CPP)

Time: Thursday 15:00–18:00 Location: MA 004

Topical Talk O 88.1 Thu 15:00 MA 004

Time-resolved chiroptical probes to track spin & light polarization in solution-processable semiconductors — •Sascha Feldmann — Harvard University, Cambridge, MA, USA

Chiral solution-processable semiconductors based, for example, on small molecules, polymers or halide perovskites offer an exciting new avenue to simultaneously control charge, spin and light using a single material. This could enable efficient spin-optoelectronic devices ranging from displays and holography to detectors, and even applications in quantum information technology.[1] In this talk, I will give an overview of our recent efforts to understand the underlying mechanisms by developing novel time-resolved chiroptical spectroscopy techniques.

By pushing broadband circular dichroism to diffraction-limited spatial and 15 fs time resolution, we create a spin cinematography technique to witness the ultrafast formation of spin domains in halide perovskite films due to local symmetry breaking and spin-momentum locking.[2] In terms of circularly polarized photoluminescence (CPL), I will first explain the fundamentals and artifacts involved in measuring CPL reliably and introduce an open-access methodology and code to do so [3]. I will conclude by showing our most recent development of a transient broadband full Stokes vector polarimetry with unprecedented time and polarization resolution to track the emergence of chiral light emission [to be submitted].

[1] Nature Reviews Materials 8, 365 (2023)
[2] Nature Materials 22, 977 (2023)
[3] Advanced Materials 44, 2302279 (2023)

O 88.2 Thu 15:30 MA 004

Nonlinear Pathways for Coherent Control of Lead Halide Perovskite Lattices — •Sebastian F. Maehrlein — Fritz Haber Institute of the Max Planck Society, Berlin

Lead halide perovskites (LHPs) constitute a vast and highly diverse library of emerging semiconductors. So far, to tailor their optoelectronic properties, the material science community mainly focused on changing the static design of the perovskite lattice by tuning the chemical composition or morphology. Meanwhile, the full potential for dynamic phonon-driven ultrafast material control, as successfully applied for oxide perovskites, has rarely been exploited.

I will present a summary of linear and nonlinear, phononic and photonic, excitation pathways to coherently control lattice vibrations with the help of intense THz fields. This comprehensive toolset not only allows to drive also non-IR active modes, but additionally unlocks phonon phase-sensitive lattice trajectory control. In prototype MAPbBr3 and CsPbBr3, we demonstrate coherent control of the octahedral twists [1], which act as structural order parameter and modulate the optical bandgap. Moving to more complex systems, we unveil counterintuitive lattice coherences in mixed 4-cation LHPs, proving the versatility of our method and providing active feedback to the design of novel energy materials.

We acknowledge fruitful collaborations with the groups of X.-Y. Zhu (Columbia U.), T. Kampfrath (FU Berlin), and S. Mathur (U. of Cologne).

[1] Frenzel et al., Sci. Adv.9, eadg3856 (2023)

O 88.3 Thu 15:45 MA 004

Confined Excitons in Lead Halide Perovskite Quantum Dots — •Lena Stickel, Anja Barfüsser, Quinten A. Akkerman, and Jochen Feldmann — Chair for Photonics and Optoelectronics, Nano-Institute Munich and Department of Physics, Ludwig-Maximilians-Universität (LMU), Königinstr. 10, 80539 Munich, Germany

In the past years, lead halide perovskite quantum dots (LHP-QDs) have gained massive attention, due to their unique optoelectronic properties.[1] We discuss sphere-like LHP-QDs, which exhibit distinct resonances in their absorption spectra.[2] By comparing experimental data with model calculations based on weak and strong confinement, the origin of these resonances was investigated. Pump-probe experiments show bleaching and induced absorption signals, which we assign to excitonic and biexcitonic transitions.[3] We further use these well-defined excitonic QDs to study the interaction between LHP-QDs and functionalized ligands.

[1] A. Dey et al. ACS Nano 2021, 15, 10775-10981.
[2] Q. A. Akkerman et al. Science 2022, 377, 1406-1412.
[3] A. Barfüßer et al. Nano Lett. 2022, 22, 8810-8817.

O 88.4 Thu 16:00 MA 004

Two-Dimensional Electronic Spectroscopy from First Principles — •Jannis Krumland[1,2], Michele Guerrini[1], Antonietta De Sio[1], Christoph Lienau[1], and Caterina Cocchi[1,2] — [1]Carl von Ossietzky Universität Oldenburg, Physics Department and Center for Nanoscale Dynamics (CeNaD), D-26129 Oldenburg, Germany — [2]Humboldt-Universität zu Berlin, Physics Department and IRIS Adlershof, D-12489 Berlin, Germany

In recent decades, two-dimensional electronic spectroscopy has been established as an experimental tool that can provide unprecedented insight into ultrafast light-matter interaction. Employing three to four concerted laser pulses, this technique is able to map out the third-order polarizability of molecules and extended systems, which contains rich information about nonlinear optical properties as well as vibronic excited-state dynamics following photoexcitation. Here, we present a first-principles approach to the simulation of two-dimensional spectra based on real-time time-dependent density functional theory and Ehrenfest molecular dynamics, applying it to prototypical molecules such as benzene and pyrene [1]. In contrast to other theoretical schemes, our approach does not require any external parameters and thus offers more predictive power. Several numerical techniques are employed to mitigate the computational complexity, making it manageable even for larger systems that are out of reach with other atomistic methods.

[1] J. Krumland et al., arXiv:2308.09062 (2023)

O 88.5 Thu 16:15 MA 004

Excited state symmetry breaking and solvation in quadrupolar dyes — •Katrin Winte[1], Somayeh Souri[1], Daniel Lünemann[1], Fulu Zheng[2], Mohamed Madjet[2], Teresa Kraus[3], Elena Mena-Osteritz[3], Peter Bäuerle[3], Sergei Tretiak[4], Antonietta De Sio[1], and Christoph Lienau[1] — [1]Oldenburg University, Germany — [2]Bremen University, Germany — [3]Ulm University, Germany — [4]Los Alamos National Laboratory, USA

Quadrupolar acceptor-donor-acceptor (A-D-A) dyes represent a versatile and chemically tunable class of prototypical molecular systems for exploring photo-induced charge transfer processes. Their optoelectronic properties are governed by an interplay between electronic tunneling between two arms and vibronic coupling to high frequency modes in each arm. In polar solvents, optical excitation results in a pronounced solvatochromism thought to arise from a light-induced charge localization inside the molecule, induced by an interplay between intramolecular charge separation and solvation[1]. So far, both processes could not be distinguished experimentally. Here, we report the first observation of the vibronic-coupling induced nonadiabatic charge separation in A-D-As. By comparing pump-probe and 2DES spectra recorded with 10fs time resolution in polar and nonpolar solvents, we demonstrate coherent vibrational wavepacket motion during the first 100fs that is largely unaffected by solvation. Our results give evidence for a vibronic-coupling induced double-minimum potential energy surface inducing spontaneous symmetry breaking and charge separation after photoexcitation. [1] E. Vauthey, J. Phys. Chem. Lett. 13,2064 (2022).

O 88.6 Thu 16:30 MA 004

THz Control of Coherent Phonon Dynamics in Low-Dimensional Hybrid Perovskites — •Joanna M. Urban[1], Marie Cherasse[1], Michael S. Spencer[1], Maximilian Frenzel[1], Charlotte Berrezueta Palacios[2], Gaelle Trippe-Allard[3], Abdelaziz Jouaiti[4], Sylvie Ferlay[4], Emmanuelle Deleporte[3], Stephanie Reich[2], Martin Wolf[1], and Sebastian F. Maehrlein[1] — [1]Fritz Haber Institute of the Max Planck Society, Berlin, Germany — [2]Institute of Experimental Physics, Freie Universität Berlin, Germany — [3]Université Paris-Saclay, ENS Paris-Saclay, CentraleSupélec, CNRS UMR 9024, LuMIn, 91190 Gif-sur-Yvette, France — [4]Université de Strasbourg-CNRS, UMR 7140, France

Charge carrier-phonon interaction governs the outstanding optoelectronic properties of hybrid lead halide perovskites (LHPs). Understanding their complex vibrational dynamics is crucial for harnessing their full potential. Recently, we used intense THz pulses to nonlinearly drive octahedral twist modes in 3D LHPs, demonstrating coherent lattice control at ultrafast timescales [1]. Low-dimensional hybrid LHPs combine the intriguing properties of the soft, polar, and anharmonic lattice with quantum confinement effects arising from the reduced dimensionality. We study quasi-2D layered Ruddlesden-Popper perovskites and 1D hybrid perovskite-like metal halides by THz Kerr Effect spectroscopy and analyze the changes of lattice dynamics with dimensionality reduction, towards a better understanding of exciton self-trapping and charge carrier screening.

References: [1] Frenzel et al., Sci. Adv.9, eadg3856 (2023)

O 88.7 Thu 16:45 MA 004

Self-Trapped Exciton Emission in Two Families of Antimony and Bismuth Halide Perovskites

— •Lukas Gümbel[1], Philip Klement[1], Meng Yang[2], Sangam Chatterjee[1], and Johanna Heine[2] — [1]Institute of Experimental Physics I and Center for Materials Research, JLU Gießen, Germany — [2]Department of Chemistry and Material Sciences Centre, PU Marburg, Germany

Main group metal halide materials are currently explored for a variety of applications including solar cells, but also light emitting devices (LED), lasers, sensing, and photo-catalysis. They promiss less harmful alternatives to the prominent lead halide perovskites. This study investigates the optical properties of antimony and bismuth halide compounds. Temperature-dependent photoluminescence spectroscopy reveals the electron-phonon coupling andyields a Huang-Rhys factor in trhe range of 5 to 22. The broad emission bands and large Stokes shifts suggest self-trapped exciton (STE) emission, linked to an interaction between the photogenerated electron-hole pairs and the lattice. The intricate interplay of factors like ground and excited state distortion, lattice softness, and electron-phonon coupling necessitates deeper understanding. A systematic analysis contributes to establishing the general structure-property relationships for STE emission in such metal halide perovskite-derivate materials. Additionally, the study delves into the diffusion of self-trapped excitons through temporal and spatial resolved photoluminescence, enhancing comprehension of emission processes.

O 88.8 Thu 17:00 MA 004

Direct observation of ultrafast lattice distortions during exciton-polaron formation in lead halide perovskite nanocrystals

— •Hélène Seiler[1,2], Zahn Daniela[1], Victoria C.A. Taylor[1], Maryna I. Bodnarchuk[3], Yoav W. Windsor[1,4], Maksym V. Kovalenko[3,5], and Ralph Ernstorfer[1,4] — [1]Fritz Haber Institute, Berlin, Germany — [2]Freie Universität Berlin, Berlin, Germany — [3]EMPA, Dübendorf, Switzerland — [4]Technische Universität Berlin, Berlin, Germany — [5]ETHZ, Zürich, Switzerland

We have employed femtosecond electron diffraction (FED) to directly measure the sub-picosecond lattice dynamics of weakly confined CsPbBr3 nanocrystals following above-gap photoexcitation. The data reveal a light-induced structural distortion appearing on a time scale varying between 380 and 1200 fs depending on the excitation fluence. We attribute these dynamics to the effect of exciton-polarons on the lattice and the slower dynamics at high fluences to slower sub-picosecond hot-carrier cooling, which slows down the establishment of the exciton-polaron population. Further analysis and simulations show that the distortion is consistent with motions of the [PbBr3]- octahedral ionic cage, and closest agreement with the data is obtained for Pb-Br bond lengthening.

O 88.9 Thu 17:15 MA 004

Structural Dynamics during Excimer Formation in Fluorinated Zinc-Phthalocyanine Thin Films

— •Sebastian Hammer[1], Laurenz Kremeyer[1], Tristan Britt[1], Maximilian Rödel[2], Jens Pflaum[2,3], and Bradley Siwick[1] — [1]Departments for Physics and Chemistry, McGill University, Montreal, QC H3A 2K6, Canada — [2]Experimental Physics VI, University of Würzburg, 97074 Würzburg — [3]CAE (Center of Applied Energy Research) Bayern,, 97074 Würzburg

In molecular solids, the coupling of charge-transfer and Frenkel states facilitated by inter-molecular vibrational modes can lead to the formation of so called excimer states [1]. The formation of these energetically low lying states is accompanied by a significant structural deformation of the local inter-molecular geometry.

In this contribution we examine the dynamics of the structural deformation during the excimer formation in polycrystalline α-zinc-phthalocyanine thin films by means of ultrafast electron diffraction. Our findings show that the geometric relaxation follows a two-step process (300 fs and $\approx$ 15 ps) and the final geometry is stable beyond 300 ps. Tuning the inter-molecular interaction by means of molecular fluorination reveals that the time-scales of the structural relaxation process are critically dependent on the local energetic environment.

Funding from the DFG (Project 490894053) is gratefully acknowledged.

[1] Bialas et al. *J. Chem. Phys. C.* **126** 4067-4081 (2022)

O 88.10 Thu 17:30 MA 004

Interrelation between excimer dynamics and crystal structure of molecular solids: The case of perylene and perfluorotetracene

— •Dominik Muth, Anton Krüger, Sebastian Anhäuser, Daniel Bischof, Gregor Witte, and Marina Gerhard — Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Germany

Excimer formation in organic semiconductors has been known for approximately 70 years. The phenomenon has, however, recently attracted increased interest due to potential applications in the fabrication of organic white light emitting diodes. Gaining insight into the process of excimer formation in molecular solids and controlling the excimer properties via the intermolecular arrangement is therefore of great interest, also from a fundamental point of view.

In this work, we investigate the excimer dynamics in single crystals of two organic semiconductors, i.e. the prototypical material perylene as well as perfluorinated tetracene via time resolved photoluminescence spectroscopy. For both materials, two different polymorphs are studied, providing insight into the influence of the molecular packing on the formation of excimers. Beside the excimer signatures, resolving the dynamics on a picosecond time scale allows us to explore short-lived higher energetic features, which potentially originate from precursor states of excimers. Varying the temperature from 10 to 295 K as well as determining the polarization of the emitted signatures reveals thermal barriers for the population of certain states and the orientation of the underlying transition dipole moments.

O 88.11 Thu 17:45 MA 004

Calculation of Diffusion Properties of Molecular Excitons based on Static Optical Spectra

— •Chris Rehhagen and Stefan Lochbrunner — University of Rostock, Institute of Physics

The understanding of the mobility of molecular excitons is fundamental for the use of molecular systems in organic solar cells. Especially a small diffusion length is a bottleneck still limiting the efficiency of light harvesting devices. Often, the diffusion constant of molecular excitons is determined by experimental methods observing e.g. exciton-exciton interaction or quenching processes. Additionally, advanced theoretical tools are used for prediction. In both cases, the effort is significant. In this work, we present a method to predict the exciton diffusion constant using static absorption and emission spectra in combination with basic geometric information of the system. Based on Försters theory the diffusion constant can be calculated from the spectral overlap and the electronic coupling. Both properties can be determined from static spectra based on the methods given in the scientific literature. We analyze these methods in detail. Then, the results are compared with experimentally determined diffusion constants in four different PBI-based solid state systems investigated in our group previously, including one-dimensional aggregates, extended nanoparticles and single crystals. In all cases, we find consistency between the experimental results and our prediction.