HL 46: Ultra-fast Phenomena II

Time: Thursday 15:00–17:15 Location: POT/0051

HL 46.1 Thu 15:00 POT/0051

Ultrafast study of out-of-plane charge carrier diffusion in perovskite thin films via pump-probe sSNOM — •Daniel Sandner[1], Branden Esses[2], Zhao Yang[3], Kai Zhu[3], Joseph Berry[2,3], Hristo Iglev[1], and Markus Raschke[2] — [1]Laser- and X-ray physics E11, TU Munich — [2]CU Boulder — [3]NREL

Despite substantial evidence for polaron formation in lead halide perovskites (LHPs), which exhibit excellent photovoltaic performance, the role of polarons in transport remains unclear. We've measured diffusion with high spatial resolution by monitoring the carrier density at the top of a thin film via the tip-localized response in pump-probe mIR-sSNOM, while exciting the sample from below. Due to the small penetration depth of the pump beam, most electrons and holes are initially located at the bottom of the perovskite layer. Consistent with previous studies, we find local variations in the diffusion coefficient. To link transport and local structure, we employ a vibrational mode as an indicator of lattice stiffness and polaron formation [JACS 2024, 146(29), 19852-19862].

HL 46.2 Thu 15:15 POT/0051

Coherent exciton-phonon coupling and many body interactions in halide perovskites probed by 2D electronic spectroscopy. — •Mohsin Sayar[1], Katrin Winte[1], Davide Caratti[2], David Cahen[2], Christoph Lienau[1], and Antonietta De Sio[1] — [1]Carl von Ossietzky Universität, Oldenburg, Germany. — [2]Weizmann Institute of Science, Rehovot, Israel

Exciton-phonon interactions are central to the unique optoelectronic properties of halide perovskites. Here we use temperature-dependent two-dimensional electronic spectroscopy (2DES) with 10 fs time resolution to study the exciton dynamics in bulk $CH_3NH_3PbBr_3$ crystals. The 2DES maps distinguish between exciton and free-carrier-induced contributions to the near-band-edge optical nonlinearity, revealing distinct signatures of exciton-exciton and exciton-carrier many-body interactions. The ultrafast dynamics further reveal coherent low-frequency phonon oscillations at $40cm^{-1}$ and $67cm^{-1}$, corresponding to Pb-Br-Pb bending and stretching modes that most strongly couple to the exciton. Additionally, we observe faster, 105 fs exciton amplitude oscillations across all three crystal phases, arising from coherent population oscillations between 1s and 2p excitonic states, off-resonantly driven by the low-frequency coherent phonon fields in the crystal. We rationalize these results within a phenomenological model accounting for both exciton-phonon coupling and 1s-2p exciton coupling via the phonon fields. Preliminary polarization-resolved 2DES data show that these phonon-induced exciton oscillations are retained upon spin-selective excitation.

Invited Talk HL 46.3 Thu 15:30 POT/0051

Antisymmetric vibrations in the excited state dynamics of quadrupolar dyes — Somayeh Souri[1], Katrin Winte[1], Daniel Lünemann[1], Daniel Timmer[1], Elena Mena-Osteritz[2], Sergei Tretiak[3], Christoph Lienau[1], and •Antonietta De Sio[1] — [1]Universität Oldenburg — [2]Universität Ulm — [3]Los Alamos National Laboratory

Non-equilibrium dynamics following photoexcitation in molecular materials arise from a complex interplay of electronic and vibrational motion, with antisymmetric vibrations playing a key role in ultrafast nonadiabatic dynamics, such as at conical intersections. Their direct spectroscopic identification is, however, challenging, since these modes are often Raman inactive and only weakly affect optical transitions. Here, we show experimental signatures of vibronic coupling to antisymmetric modes in the ultrafast symmetry-breaking dynamics of a quasi-quadrupolar dye[1,2] using two-dimensional electronic spectroscopy (2DES). The sub-50-fs 2DES maps reveal an asymmetric peak pattern with characteristic low-energy cross-peaks. We show that these peaks arise from stimulated emission from a double-minimum excited state potential energy surface induced by vibronic coupling to a ~1430 cm-1 antisymmetric mode[2]. Phenomenological essential state model simulations support the results. Our findings show that 2DES with sub-cycle vibrational resolution is a powerful method for identifying antisymmetric modes in the excited state dynamics prior to intramolecular vibrational relaxation and solvation. [1] Winte et al, Nature Chemistry 17, 1742 (2025); [2] Souri et al, submitted (2025)

15 min. break

HL 46.4 Thu 16:15 POT/0051

Investigating exciton dynamics and exciton–exciton interactions via optical two-dimensional photoelectron spectroscopy — •Luisa Brenneis[1], Matthias Hensen[1], Julian Lüttig[2], and Tobias Brixner[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Department of Physics, University of Ottawa, 150 Louis-Pasteur Pvt, Church St, Ontario K1N 6N5, Canada

Action-detected two-dimensional (2D) electronic spectroscopy has become a powerful technique to resolve exciton dynamics by measuring an incoherent signal proportional to the excited-state population generated by a multi-pulse sequence. However, processes that alter the excited-state population after the system's interaction with the pulse sequence, such as exciton–exciton annihilation, can obscure coupling signatures and single-exciton dynamics [1]. In optical 2D photoelectron spectroscopy (2DPES), typically a four-pulse sequence excites the system, followed by a time-delayed ionization pulse [2]. Here, we show how to disentangle exciton dynamics and interactions by varying the ionization pulse time delay. Exemplary simulations of a weakly coupled dimer demonstrate that short ionization delays reveal coupling signatures and single-exciton energy transfer, whereas longer delays reveal exciton–exciton annihilation. This concept is particularly promising for nanoscale surface studies, where 2DPES combined with photoemission electron microscopy enables spatially resolved exciton mapping.

[1] M. Bruschi et al., Phys. Chem. Lett. 14, 30, 6872 (2023).
[2] D. Uhl et al., Optica 8, 10, 1316 (2021).

HL 46.5 Thu 16:30 POT/0051

Ab initio Theory of Coherent Phonon Damping in Semimetals — •Yiming Pan and Fabio Caruso — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24118 Kiel, Germany

Coherent phonon plays an important role in the structural properties of the crystal lattice and ultrafast light-induced phase transition. Following its excitation, atoms oscillate coherently along the excited modes with decaying amplitudes. This dynamical process is commonly modeled with damping oscillators with phenomelogical damping rates. In this work, we derive this model by employing quantum kinetic equations [1], and attribute the damping rate and frequency renormalization of coherent phonon to the imaginary and real parts of the phonon self-energy. To valdiate our approach, we perform first-principles calculation of the damping rate of A_{1g} phonon arising from electron-phonon coupling and phonon-phonon coupling in semimetals Bi and Sb. The numerical results agree with available temperature- and fluence-dependent experimental data, thereby providing a predictive framework for determining the timescales of structural dynamics in driven solids.

[1] Y. Pan *et al.*, arXiv:2502.01529

HL 46.6 Thu 16:45 POT/0051

Probing Ultrafast Electronic and Lattice Dynamics simultaneously at the Atomic Scale with Time-Resolved Diffraction Anomalous Fine Structure (TR-DAFS) — •Moritz Meissner[1,2,6], T. C. Rossi[2], M. Rössle[2], C. Petersen[3], H. von Wenckstern[3], R. Mandal[4], M. Levantino[5], and R. M. van der Veen[2,6] — [1]Paul-Drude-Institut für Festkörperelektronik — [2]Helmholtz Zentrum Berlin — [3]Universität Leipzig — [4]Institut des materiaux de Nantes Jean Rouxel — [5]European Synchrotron Radiation Facility — [6]Technische Universität Berlin

This work presents the first successful demonstration of Time-Resolved Diffraction Anomalous Fine Structure (TR-DAFS) measurements carried out in a pump-probe (stroboscopic) scheme. We show that TR-DAFS can directly probe ultrafast structural and electronic dynamics in crystalline materials. Investigating Zinc oxide (ZnO) enables direct comparison between TR-DAFS at the Zn K-edge with time-resolved X-ray absorption spectroscopy (TR-XAS) data. TR-DAFS represents a leap forward in the study of photoexcited materials at the atomic scale by providing access to different aspects of lattice dynamics in resonant and non-resonant parts of the spectrum. Preliminary ab initio calculations show that the electronic changes visible in the resonant

part of the spectrum are associated with an increase of carrier temperature in the photoexcited state. This dual sensitivity to electronic and lattice degrees of freedom makes TR-DAFS a game-changer in investigating ultrafast processes in complex materials and heterostructures as represented by the results of this work.

HL 46.7 Thu 17:00 POT/0051

Theoretical Modeling of Ultrafast Phase Transitions from the Femtosecond to the Picosecond Scale — Stefano Mocatti, Giovanni Marini, Pierluigi Cudazzo, and •Matteo Calandra — Department of Physics, University of Trento, Via Sommarive 14, 38123 Povo, Italy

In this talk, I will introduce a theoretical approach to ultrafast phase transitions that captures both electron/hole and phonon dynamics following laser pumping, on time scales ranging from a few femtoseconds to several picoseconds after irradiation.

At short times, the method relies on solving the Bloch equations coupled to Ehrenfest dynamics. It includes the electric field of the pump explicitly, as well as carrier-carrier, carrier-phonon, and phonon-phonon scattering, treated entirely from first principles.

At longer times before recombination, when carrier-carrier interactions generate a photoexcited quasi-equilibrium electron-hole plasma, the approach is based on a constrained density-functional perturbation theory (cDFPT) scheme that accounts for the presence of holes in the valence band and electrons in the conduction band (two-Fermi-level approach). In this framework, the calculation of forces, phonon dispersion, and carrier-phonon coupling becomes possible, as well as molecular dynamics with machine-learning potentials in the presence of an electron-hole plasma.

I will showcase applications of the method to several materials.

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