

HL 1: Focus Session: When theory meets experiment: Hybrid halide perovskites for applications beyond solar

Hybrid halide perovskites are by now well-established solar absorber and emitter materials, with power conversion efficiencies of single-cell devices exceeding 20 percent. We have observed - with notable exceptions - a widening gap between experimental and theoretical efforts in the literature on halide perovskites. Further, a large fraction of the literature focuses on properties relevant for optoelectronic applications, while we envision a much wider scope for these materials, e.g in spintronic and electrochemical applications. The purpose of this focus session is to provide a platform for theorists and experimentalists working in this field, to interact, present state-of-the-art methods, and exchange their ideas on future directions for this technologically relevant class of materials beyond the current focus on optoelectronics.

Organizers: Linn Leppert (University of Twente) and Felix Dreschler (TU München)

Time: Monday 10:00–12:45

Location: H4

Invited Talk HL 1.1 Mon 10:00 H4
Phonon Screening of Excitons in Halide Perovskites and Beyond — ●MARINA FILIP — University of Oxford, Department of Physics

The interaction of photoexcited bound electron-hole pairs (excitons) is screened by both electrons and by polar phonons. For organic-inorganic lead-halide perovskites, theoretical and experimental evidence suggests that ionic vibrations have an important contribution to the dielectric screening [1,2]. However, state of the art GW/BSE methodology for studying electronic and optical excitations does not capture phonon screening effects. In this talk I will present our recently developed framework based on GW/BSE, to include phonon screening effects [3]. I will show that phonon screening contributes to significantly reduce the exciton binding energy, and demonstrate this effect for lead halide perovskites, CsPbX₃ (X = Cl, Br, I), as well as other well known semiconductors and insulators. Furthermore, I will show our generalization of the Wannier-Mott model to include phonon screening effects, and discuss general trends for the phonon screening contribution to the exciton binding energy.

[1] Miyata et al, Nat. Phys. 11, 582 (2015) [2] Umari et al, JPCL, 9, 3, 620 (2018) [3] Filip, Haber & Neaton, PRL, in press (2021)

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Invited Talk HL 1.2 Mon 10:30 H4
Anharmonic semiconductors - Lessons Learned from Halide perovskites — ●OMER YAFFE — Weizmann Institute of Science, Rehovot, Israel

In semiconductor physics, the dielectric response, charge carrier mobility and other electronic material properties at finite temperatures, are always treated within the framework of the harmonic approximation. This approach is very successful in capturing the properties of tetrahedrally bonded semiconductors such as silicon and GaAs.

In my talk, I will show that halide perovskites are fundamentally different due to their strongly anharmonic lattice dynamics. Large amplitude, local polar fluctuations induced by lattice anharmonicity localize the electronic states and enhance the screening of electric charge within the material. In other words, in some aspects, halide perovskites behave more like a liquid than a crystalline solid. I will also discuss the implications of these findings on other families of semiconductors such as organic and rock-salt semiconductors.

Invited Talk HL 1.3 Mon 11:00 H4
Exciton structure symmetry analysis for quantum-well layered halide perovskites and charge-energy transfer in presence of π -conjugated organic chromophores — ●CLAUDIO QUARTI — Laboratory for Chemistry of Novel Materials, University of Mons

2D layered halide perovskites are surging as interesting materials for opto-electronic applications. These systems are characterized by a quantum-well structure, with a semiconducting halide perovskite frame sandwiched between organic insulating spacers, the spatial confinement stabilizing tightly bound excitons. Still, full understanding of the native electronic and excitonic properties of layered halide per-

ovskites is inherently hard to achieve, as many physical mechanisms contribute to complicate the scenario, including dielectric confinement, structural distortions, Spin-Orbit-Coupling (SOC), etc. Here, I review the electronic and excitonic structure of 2D layered halide perovskites, adopting group theory symmetry analysis. This highlights the analogies and differences in the atomic contributions on the single particle band structure, as compared to the 3D case, with SOC inherently included in the analysis. I will then consider the interaction between the organic spacers and the inorganic semiconducting frame in the case of a type II heterointerface, as obtained via incorporation of π -conjugated molecular moieties as organic spacers. With reference to tetrazine-based layered halide perovskite, I discuss several photoexcitation decay channels, with clear distinction between charge, singlet- and triplet-energy transfer.

15 min. break.

Invited Talk HL 1.4 Mon 11:45 H4
Solid state ionics of hybrid halide perovskites: equilibrium situation and light effects — ●ALESSANDRO SENOCRATE^{1,2}, GEE YEONG KIM¹, TAE-YOUL YANG¹, GIULIANO GREGORI¹, MICHAEL GRÄTZEL^{1,2}, and JOACHIM MAIER¹ — ¹Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany — ²École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

In recent years, hybrid halide perovskites have been attracting great attention due to their exceptional photo-electrochemical properties. When used as light-harvesters in solar cells, device efficiencies exceeding 25 % can be realized. We showed that a deeper understanding of (i) functionality, (ii) stability, as well as (iii) the possibility to improve the performance require a thorough insight into non-stoichiometry and ion transport. In this contribution, we study the nature of the ionic conductivity in methylammonium lead iodide (MAPbI₃), the archetypal halide perovskite, by means of a great number of electrochemical and nuclear magnetic techniques. To aid the experimental investigation, we include detailed defect chemical modelling describing the effects of varying iodine partial pressure (stoichiometry) and dopant content. By extending this study to the situation under illumination, we observe a striking enhancement of ionic conductivity by more than 2 orders of magnitude in MAPbI₃, alongside the expected increase in electronic conductivity. Such analyses are then extended to other halide perovskite compositions. While discussing these results, a mechanistic explanation of this astonishing phenomenon arises, which has relevance for photo-stability and photo-demixing processes.

Invited Talk HL 1.5 Mon 12:15 H4
Unifying Ultrafast Polarization Responses of Lead Halide Perovskites via Two-Dimensional Optical Kerr Effect — ●SEBASTIAN F. MAEHRLEIN — Columbia University, New York, USA — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

The microscopic mechanism behind the outstanding optoelectronic properties of lead halide perovskites (LHPs) may lead to novel design principles for defect tolerant semiconductors, but is still highly debated. Previous studies, investigating the LHPs' ultrafast polarization response by the optical Kerr effect lead to dynamic screening models, which suggest charge carrier protection by large polarons and/or liquid-like screening.

Here, we finally decode the variety of nonlinear polarization sig-

nals by developing two-dimensional optical Kerr effect (2D-OKE) spectroscopy. We unveil a surprisingly unified origin: Both (inorganic and hybrid) LHP responses are governed by nonlinear mixing of anisotropic and highly dispersive light propagation near the optical band gap [1]. Based on the 2D-OKE fingerprint, we quantify dispersion anisotropy, follow phase transitions and trace lattice parameters of hybrid alloyed LHPs; supported by a comprehensive four-wave-mixing model. More-

over, our findings raise the awareness in all types of polarization sensitive pump-probe experiments and their modeling, where oscillatory signals are commonly assigned to coherent low-energy excitations (e.g. phonons, magnons, etc.). The presented works were mainly performed with L. Huber, F. Wang, and P.P. Joshi at X.-Y. Zhu group (Columbia U). [1] S. F. Maehrlein et al., DOI:10.1073/pnas.2022268118