

# **Structural Dynamics in Lead-Halide Perovskites from Molecular Dynamics Calculations**

David A. Egger<sup>1,2</sup>

<sup>1</sup> *Department of Materials and Interfaces, Weizmann Institute of Science,  
Rehovoth 76100, Israel.*

<sup>2</sup> *Institute of Theoretical Physics, University of Regensburg,  
93040 Regensburg, Germany*

david.egger@weizmann.ac.il

The optical and transport properties of lead-halide perovskites (LHPs) have been used as a basis for new solar cell technologies showing record improvements in power-conversion efficiencies. In the search for the microscopic origins of this success, the outstanding electronic-structure properties of LHPs are, of course, one important ingredient. However, many recent studies suggest that structurally dynamic effects, going strongly beyond small harmonic vibrations, are active already at room temperature and standard operating conditions. These effects are currently speculated to play an essential role in explaining the outstanding optical and charge-transport properties of LHPs.

Here, we will explore the issue of structural dynamics on the basis of first-principles calculations. Specifically, our results from molecular dynamics (MD) based on density functional theory will be presented. This allows for a temperature-dependent analysis of trajectories and, when combined with polarizability calculations, provides spectroscopic quantities accessible also experimentally.

First, the impact of optical phonons on charge-transport will be discussed. Data from far-infrared spectroscopy measurements of different LHPs show a strong broadening and anharmonicity of the lattice vibrations, indicating that complex vibrational features are active at room temperature. When these data are combined with appropriate models, estimates for the charge-carrier mobilities due to optical phonon scattering can be extracted. We find that the magnitude of these estimated mobilities is well within the

range of reported experimental data for single crystals, but that their temperature-dependence is not.

Second, our recent findings on local polar distortions in hybrid organic-inorganic and all-inorganic LHPs will be discussed. Results from low frequency Raman scattering and MD simulations show a strong central peak in both hybrid and all-inorganic LHPs, which suggests that anharmonic, local polar fluctuations are intrinsic to the LHP structure and not unique to perovskites with dipolar organic cations. A detailed analysis of our MD simulations and experimental data indicates that these polar fluctuations occur on timescales of a few hundred femtoseconds and do not contradict a fully cubic lattice on average. We also find that head-to-head cationic motion is coupled to anionic face expansions in driving the local polar fluctuations in LHPs.