

Implications of Structural Anharmonicity for Optoelectronic Properties in Halide Perovskites

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Halide perovskites (HaPs) are highly promising materials for solar cells and other optoelectronic devices. These compounds are not only interesting technologically, but also very curious scientifically and present us with several curious puzzles. In particular, it has been recognized that HaPs show significant structural disorder and anharmonicity in their nuclear vibrations already at room temperature. These phenomena were examined on the basis of results obtained in multiple complementary experimental and theoretical techniques. In view of all this evidence for such complex structural dynamics, disorder and anharmonicity, one must ask how HaPs can even appear as highly efficient optoelectronic materials in devices such as thin-film solar cells?

Here, I will use theoretical calculations, mostly based on molecular dynamics (MD) and density functional theory (DFT), in order to explore the origin as well as the consequences of the structural anharmonicity and disorder in HaPs. First, it will be discussed what consequences anharmonic effects could in principle have for vibrational observables including phonon frequencies and lifetimes. For HaPs, it will then be shown that while there are no large qualitative consequences for the vibrational frequencies due to anharmonicity, phonon lifetimes are still ultra-short, in agreement with recent experimental and theoretical work. Since they are much smaller than the phonon lifetimes in bulk Si in a similar temperature and frequency range, it is concluded that the phonons in HaPs are massively anharmonic. In search for the origin of these effects we explore the role of a resonant bonding mechanism, which has been discussed for HaPs already 40 years ago, to show that nuclear displacements can lead to long-range charge density-responses and, hence, phonon-phonon interactions.

Having accepted that HaPs are highly anharmonic and dynamic structurally, I will examine the question of how it is still possible that these compounds are still excellent solar absorber materials. To this end, our MD calculations are used to define and characterize the dynamic behavior of a disorder potential for the electronic states in HaPs. Specifically, we can probe how far any instantaneous disorder induced by the nuclear dynamics is correlated in the material. Surprisingly, we find that the spatial correlations are similar to the range that has been reported for bulk Si and GaAs, which will be traced back to a dynamic shortening of their impact by means of the massive nuclear dynamics in the system. This property results in the sharp optical absorption edges and small Urbach energies that were reported for HaPs, which are highly desired properties of any solar material.

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