Specific Coherent Phonon Strongly Modulates the Band Gap of Perovskites

Mischa Bonn*

Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
* *bonn@mpip-mainz.mpg.de*

Methylammonium lead iodide perovskites are increasingly being used for high-efficiency, low-cost photovoltaics.[1] These perovskites are soft materials where thermally populated phonons lead to a large structural variability and peculiar opto-electronic properties at ambient temperature.[2] One peculiarity is the unique temperature-dependence of the optical band gap: the band gap increases with increasing lattice temperature[3], whereas thermal expansion generally leads to the opposite behavior in conventional semiconductors (silicon, gallium arsenide, etc.). Despite the presence of thermally accessible phonons at room temperature, which are responsible for many of the unique opto-electronic properties of this perovskite (and thereby photo-conversion efficiency), a fundamental understanding of how changes in temperature affect the optical properties of this material, via phonon modes has remained elusive.

To specifically address the relation between phonons and the optical band gap, we have developed a novel THz pump-optical probe experiment, which allows directly accessing the coupling between phonons and the optical gap. Following ultrafast, broadband THz excitation, we monitor the band edge absorption at room temperature. We find surprisingly strong coupling between specifically the 1 THz (33cm^{-1}) phonon and the optical band gap. The coherent excitation of the phonon leads to an oscillating band gap: the phonon transiently changes the color of the perovskite. Quantitative modeling shows that population of this phonon fully captures the macroscopic temperature dependence of the material: the temperature-dependent optical properties can be fully accounted for by the thermal excitation of this 1 THz phonon.

Our results thus provide a clear picture how one phonon governs one of the key macroscopic properties of this perovskite, and likewise, demonstrate a broadly applicable approach to study isolated phonon behaviors in various semiconductors without perturbation of photo-carriers.

(1) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. *Nat. Photonics* **2014**, *8* (7), 506.
(2) Quarti, C.; Mosconi, E.; De Angelis, F. *Chem. Mater.* **2014**, *26* (22), 6557.
(3) Milot, R. L.; Eperon, G. E.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. *Adv. Funct. Mater.* **2015**, *25* (39), 6218.
(4) Kim, H; Cánovas, E.; Karakus, M; Mics, Z.; Grechko, M.; Turchinovich, D.; Parekh, S.H.; Hunger, J.; Bonn, M., *Nat. Comm.* **2017**, in print