Ultrafast Photophysics of Hybrid Lead Halide Perovskites Using Sub-10 Femtosecond Pump-Probe Spectroscopy

Tufan Ghosh

Institute of Physical Chemistry II, Ruhr-University Bochum, 44801 Bochum, Germany

Email: tufanghosh55@gmail.com

Abstract: Hybrid lead halide perovskites (LHPs) have been emerged as an efficient material for superior solar energy conversion during the last decade, due to their following unique properties: large absorption coefficient in the visible, low charge carrier (electron/hole) recombination rates, and sufficiently long carrier diffusion length.[1-3] Understanding fundamental photophysics behind such high power conversion efficiency requires a thorough understanding of the following phenomena: dissociation excitons to free carriers, hot carriers cooling, and recombination dynamics. We use sub-10 femtosecond pump-probe spectroscopy to uncover early stages of carrier evolution in methylammonium lead iodide ($MAPbI_3$) perovskite thin films.[4,5] Results show that photoexcitation with laser pulses centered ~530 nm (~0.7 eV excess to that of the band gap of $MAPbI_3$) generates localized exciton (e-h pair), which subsequently dissociate to free carriers within first 20 fs. In later stages, these hot free carriers cool to the band edge by emitting optic phonons, with a time constant ~0.4 ps. Using a very high signal-to-noise ratio (S/N), we are able to detect faint periodic spectral modulation in the transient signals due to electron-phonon coupling in the material. The Fourier transform of the periodic modulation results in mainly two frequencies: ~100 and ~240 cm^{-1} assigned to the stretching of Pb-I bonds in the inorganic cage and torsions of $CH_3NH_3^+$ cation, respectively. The amplitude of the spectral modulations has been used to estimate the electron-phonon coupling strength. The estimated coupling strength falls in the weak regime and hence suggest the formation of large polarons.

References:

[1] Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051.

[2] Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. *Science* **2013**, *342*, 341–344.

[3] Manser, J. S.; Kamat, P. V. *Nat. Photon* **2014**, *8*, 737–743.

[4] Ghosh, T.; Aharon, S.; Etgar, L.; Ruhman, S. *J. Am. Chem. Soc.* **2017**, *139*, 18262–18270.

[5] Ghosh, T.; Aharon, S.; Shpatz, A.; Etgar, L.; Ruhman, S. *ACS Nano* **2018**, *12*, 5719–5725.