Perovskite nanoplatelet inhomogeneity from generalized Einstein relations between absorption and emission

Callum R. Douglass, Jisu Ryu, and David M. Jonas
Department of Chemistry, University of Colorado Boulder

It is conventionally thought that nonlinear spectroscopy techniques such as photon echoes or four-wave mixing are required to separate homogeneous and inhomogeneous broadening. Using femtosecond two-dimensional Fourier transform spectroscopy on PbS quantum dots, we have recently shown that single-molecule generalized Einstein relations allow the quantitative determination of inhomogeneous broadening form absorption and emission spectra provided first that thermal quasi-equilibrium is established on a timescale much faster than the emission lifetime and second that there is negligible energy transfer between members of the inhomogeneous ensemble [*Science Advances* **7**, eabf4741 (2021 – in press)]. This is possible because photoluminescence is a two-photon process, and thus a kind of nonlinear spectroscopy. Here, we present the single-molecule generalized Einstein relations, show how they determine the homogeneous linewidth from the Stokes' shift between absorption and emission for Gaussian spectra, and then apply them directly to the emission spectra of quasi-two dimensional perovskite nanoplatelets precisely two layers thick. Surprisingly, comparison between the absorption spectra calculated from emission spectra and the measured attenuation spectra shows that the nanoplatelet spectra are inhomogeneously broadened. Transmission electron microscopy images show that the nanoplatelets are stacked, with well-aligned edges that suggest stacking during growth in solution. The frequency shifts that result from stacking in solution indicate electronic coupling between nanoplatelets.

AFOSR grant # FA9550-18-1-0211
Controlling Energy Transfer Pathways