Optoelectronic Signatures of Positive and Negative Polarons in Two-Dimensional Lead Chloride Perovskites

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Lead halide perovskites are of interest for light-emitting applications due to the tunability of their bandgap across the visible and near-infrared spectrum (IR) coupled with efficient photoluminescence quantum yields (PLQY)[1]. It is widely speculated that photoexcited electrons and holes spatially separate into large negative (electron) and positive (hole) polarons[2]. Polarons are expected to be optically active. With the observed optoelectronic signatures expecting to show potential excited states within the polaronic potential well. From the polaron excited-state we predict that large polarons should be capable of spontaneous emission, photoluminescence, in the mid-IR to far-IR regime based on the concept of inverse occupations within the polaron potential well. Here we use density functional theory (DFT), including spin-orbit coupling interactions, and excited state dynamics treated by reduced density matrix method[3] for calculations on a two-dimensional Dion-Jacobson lead chloride perovskite atomistic model[4] as a host material for either negative or positive polarons to examine the polaronic effects[5]. Nonradiative relaxation of the excited polaronic states are computed in terms of Redfield theory[6], which is parameterized using nonadiabatic couplings between electronic and nuclear degrees of freedom. Radiative relaxation of excited polaronic states is found from Einstein coefficients for spontaneous emission. PLQY is used to determine the efficiency of polaron IR emission using rates of nonradiative recombination (k_{nr}) and radiative recombination (k_r) as $\frac{k_r}{k_r+k_{nr}}$. Here we develop evidence in support for the idea that polaron formation in lead chloride perovskites allows for IR emission and absorption.

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