Electronic Coherence and Excited-State Dynamics of Photo-Induced Polarons in Lead Halide Perovskites

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$APbX_3$ (A=Cs,Methylammonium{MA}; X=I,Br,Cl) lead halide perovskites of various morphology are of interest for light-emitting applications due to the tuneability of their bandgap across the visible spectrum and efficient photoluminescence quantum yields (PLQYs). In the excited-state it is suspected that large polarons form due to coupling of photo-excited charges to the soft perovskite lattice. Polarons are expected to display enhanced electronic coherences and longer non-radiative lifetimes due to screening of optical phonons[1]. At the same it would be expected that polaron formation would inhibit radiative recombination due to charge localization. Here we implement *ab Initio* atomistic modeling to investigate polaron photo-physics in a $CsPbBr_3$ nanocrystal (NC) passivated with organic ligands. Specifically, we model simultaneous positive and negative polarons occupation within the NC which would be analogous to a photo-excitation. For electronic basis we use spinor Kohn-Sham orbitals (SKSOs) which include relativistic corrections and the spin-orbit coupling (SOC) interaction. Non-radiative relaxation, describing population and phase relaxation, is described in terms of Redfield theory by propagating the excited-state density matrix for electronic degrees of freedom weakly coupled to a heat bath[2]. To account for changes in the potential energy surface due to polaron formation we explicitly use excited-state PESs for the non-adiabatic dynamics. Rates of population transfer are parameterized from non-adiabatic couplings between electronic and nuclear degrees of freedom and are computed 'on-the-fly'. Dephasing of electronic coherences are found within the 2nd order cumulant expansion[3]. Radiative relaxation rates of charge carriers are computed using Einstein coefficient for spontaneous emission[4]. Implications of this work will provide better understanding of polaron dynamics within lead halide perovskite materials and their implications for radiative and non-radiative recombination.

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