Examination of Photo-Induced Polarons and Machine Learned Force-Fields in Two-Dimensional Lead Halide Perovskites

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Lead halide perovskites (LHP) are of interest for light-emitting and photovoltaic applications due to the tunability of their bandgap, due to confinement and composition, across the visible and near-infrared spectrum (IR) coupled with efficient photoluminescence quantum yields (PLQY). In the excited-state, coupling of the photo-induced charges to the soft perovskite lattice is suspected to form large polarons.[1] The spatial separation of photo-induced electrons and holes inherent to polaron formation reduces the efficiency of the interband radiative recombination. Additionally, polarons are expected to show longer non-radiative lifetimes due to phonon screening.[1] Due to the size of the models investigated, we explore the use of machine learned force-fields (MLFF) to calculate the adiabatic molecular dynamics (MD) which are then used to calculate the 'on-the-fly' nonadiabatic couplings (NAC) for nonpolaronic LHPs. MLFFs are trained using on-the-fly learning which builds a force field using *ab* initio MD (AIMD) data. We find that MLFF accelerated MD provides comparable results to AIMD when the MLFF is trained in a NpT ensemble. Investigation of polaron photophysics is performed using *ab initio* atomistic modeling in a two-dimensional Dion-Jacobson lead chloride perovskite. Simultaneous negative and positive polarons are modeled within the perovskite layer analogous to a photoexcitation. Spinor Kohn-Sham orbitals (SKSO) are used for the electronic basis and include relativistic corrections and the spin-orbit coupling (SOC) interactions. Nonradiative relaxation of the excited polaronic states are computed in terms of Redfield theory[2] by propagating the excited-state reduced density matrix for electronic degrees of freedom weakly coupled to a heat bath.[3] NACs between electronic and nuclear degrees of freedom, computed 'on-the-fly', are used to parametrize the rates of population transfer.[4] The excited-state potential energy surface is used for the non-adiabatic dynamics to account for changes in the potential energy surface due to polaron formation. Einstein coefficients for spontaneous emission is used to compute the radiative relaxation rates of charge carriers.[5] Here we develop evidence that will improve the understanding of polaron dynamics in lead halide perovskites and their implications for radiative and nonradiative recombination.

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