

# Understanding Impact of Crystalline Structure on Photodynamics in Halide Perovskites: Time-Domain Ab Initio Study

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All-inorganic halide perovskites (IHPs) such as CsPbX<sub>3</sub> (X = I and Br) are considered one of the most promising candidates with enhanced stability for applications of solar cells, photo-detectors, light-emitting diodes (LEDs) compared to hybrid organic-inorganic halide perovskites that have unsatisfactory long-term stability issues. [1-3] For practical use such as LEDs, IHPs exist in the form of nanosized quantum dot (QD) structures. Unlike with the bulk structures which undergo temperature-dependent phase transitions, IHP QDs show the coexistence of multiple phases at room temperature due to the influence of surface energy and passivating ligands. [4,5] However, within the reduced dimensionality of QDs, non-radiative electron-hole recombination is one of the essential factors limiting optical property.

In this study, by performing the time-dependent density functional theory (TDDFT) [7,8] and nonadiabatic molecular dynamics (NAMD) simulation [9] on the four different phases of CsPbBr<sub>3</sub> (orthorhombic, tetragonal *I4/mcm*, tetragonal *P4/mbm*, and cubic), we theoretically investigate the phase-dependent nonradiative recombination process. The computed recombination lifetime of the CsPbBr<sub>3</sub> is a good agreement with the experiment. The nonadiabatic (NA) coupling between the band edges depends on the phase and governs the recombination dynamics. From the analysis of the ion's free volume and lattice vibration, we quantified the NA coupling in terms of lattice vibration depends on the phase, and assigned the specific phonon modes responsible for the electron-phonon interaction within the inorganic network.

## References

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