

Supplemental Material for

**“Temperature Induced Large Broadening and Blueshift in the
Electronic Band Structure and Optical Absorption of
Methylammonium Lead Iodide Perovskite”**

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Computational details

The finite temperature electronic band structure and optical absorption calculations reported in the main text have been performed using the ABINIT software package.^{1, 2} The optimized norm-conserving Vanderbilt pseudopotentials (ONCVSP)³ and the semilocal Perdew-Burke-Ernzerhof (PBE)⁴ exchange-correlation functional are used for the first-principles calculations. After the convergence test, the energy cut-off is finally chosen as 680 eV (Figure S1), and the electronic Brillouin zone is sampled as a $6 \times 6 \times 6$ grid for the unit cell. Note that due to the computational limitation, the spin-orbit coupling is neglected in this work.

The thermal expansion effect is calculated using the finite displacement method within the quasi-harmonic approximation.⁵ The electron-phonon coupling is calculated following the Allen-Heine-Cardona (AHC) theory.^{6, 7} Within the density functional perturbation theory (DFPT) framework,^{8, 9} up to second-order electronic eigenvalues in the electron-phonon coupling can be computed and the higher terms are neglected. The real part of the second-order electronic eigenvalues was calculated from the density functional perturbation theory method,^{8, 9} while the imaginary part was obtained within the scheme of Fermi-Dirac smearing with the smearing width of 0.1 eV. During the electron-phonon coupling calculations, the $6 \times 6 \times 6$ Γ -centered \mathbf{k} -point and \mathbf{q} -point grid in the first Brillouin zone with a plane-wave energy cutoff of 680 eV is used.

To calculate optical properties, we firstly choose three different methods of random phase approximation (RPA)¹⁰, GW^{11, 12} and Bethe-Salpeter equation (BSE)^{13, 14} to investigate the influence of many-body effect. In the RPA method, electrons are treated as independent particles and respond only to the total electric potential. Thus, the calculated optical absorption is the averaged value contributed by the total electric potential. While in the GW approach,^{11, 12}

electrons are treated as quasiparticles with self-energy and the propagation of quasiparticle is defined by the time-ordered Green's function. The many-body effect can renormalize the electronic band structure and accurately predict the band gap. Furthermore, in the BSE method,^{13,}¹⁴ the interactions among quasiparticles is considered and the interacting electron-hole pair is formulated in terms of two-particle propagators. In the ABINIT, to include the interacting electron-hole pair into optical absorption calculations, there are three main steps: (1) conventional density functional theory (DFT) calculations to obtain the independent Kohn-Sham orbitals and eigenvalues; (2) GW calculations to renormalize the electronic band structure and band gap; (3) and BSE calculations to include the interacting electron-hole pair into optical transition matrix and compute the optical properties within the many-body theory. During the optical absorption calculations, the plane-wave energy cutoff is 680 eV and the energy cutoff for the dielectric matrix is 272 eV. Moreover, during the BSE calculations, a small shift of 0.15 eV is used to avoid divergences in the expression for the macroscopic dielectric function.

Convergence test

Prior to performing the first-principles calculations of electronic band structure and optical absorption of cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, it is of great necessity to do the convergence test on the important quantity of plane-wave energy cutoff. In Figure S1 of the convergence test, it shows that as the energy cutoff is chosen as 680 eV, the total energy is sufficiently converged. The relatively large value of energy cutoff is mainly due to that we choose the norm-conserving pseudopotential for the first-principles calculations.

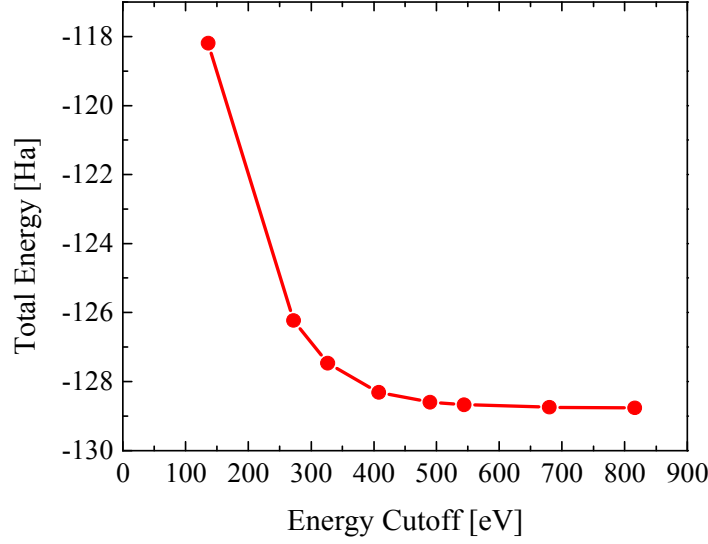


Figure S1. Convergence test of the plane-wave energy cutoff for the cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite.

Thermal expansion

The thermal expansion effect is included within the quasi-harmonic approximation (QHA). The Gibbs free energy of a solid at finite temperature T and constant pressure P is determined by⁵

$$G(T, P) = \min_V [U(V) + F(T; V) + PV], \quad (\text{S1})$$

where U is the total energy of electronic structure, F is the phonon (Helmholtz) free energy and \min function is to search for unique minimum value in the brackets by changing volume V . For each constant couple of T and P , the Gibbs free energy is the unique function of volume V and the equilibration volume can be determined by minimizing G with respect to the volume.

We have calculated the thermal expansion of cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite at constant pressure within the quasi-harmonic approximation. The calculated results show that the equilibrated lattice constant from 6.32 Å from 0 K to 6.48 Å at 500 K, in overall agreement with

literature data.^{15, 16} As temperature increases, the contribution of thermal expansion to band gap correction slightly increases. At 100 K, the band gap of opening due to thermal expansion is 20 meV and increases to 80 meV at 500 K. As for the electron-phonon coupling, it shows that its contribution to band gap opening increases from 200 meV at 100 K to 646 meV at 500 K. Since the high order terms of electron-phonon coupling and spin-orbit coupling (SOC) is neglected, the calculated band gap correction within AHC theory overestimates that of ref 15 which uses Monte-Carlo method and includes the SOC. Thus, we introduce an energy scissor to correct for such overestimation and the value of energy scissor changes from 50 meV at 100 K to 200 meV at 500 K. After introducing the energy scissor, the optical absorption peak position at finite temperature can be predicted with higher accuracy, as shown in Figure S2.

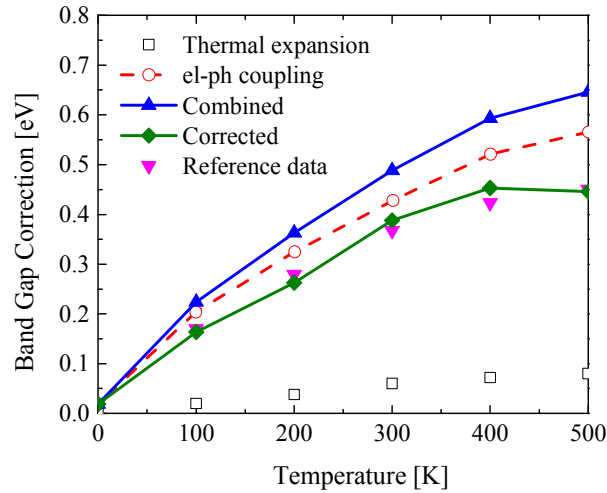


Figure S2. Temperature-dependent band gap of cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite calculated using thermal expansion only (black open square), electron-phonon coupling only within the AHC theory (red dashed-open-circle line), the combined result (thermal expansion + electron-phonon coupling, blue solid-up-triangle line) and the final result corrected with energy scissor (green solid-diamond line) in comparison with the data from ref 15 (pink down triangle).

CsPbI₃

In comparison, we also compute the temperature-dependent band gap of inorganic CsPbI₃ perovskite. The electron-phonon coupling following the AHC theory as well as the thermal expansion is considered to study the temperature influence. Within the quasi-harmonic calculations, the equilibrated lattice constant expands from 6.12 Å from 0 K to 6.30 Å at 500 K. Due to the high order terms in the electron-phonon coupling as well as the spin-orbit coupling is neglected during the first-principles calculations, an energy scissor is introduced. In Figure S3, it shows the theoretically calculated band gap change of inorganic CsPbI₃ perovskite, in comparison with ref 15. As temperature increases, it is observed that the band gap is slightly enlarged, which is similar to that of hybrid CH₃NH₃PbI₃ perovskite.

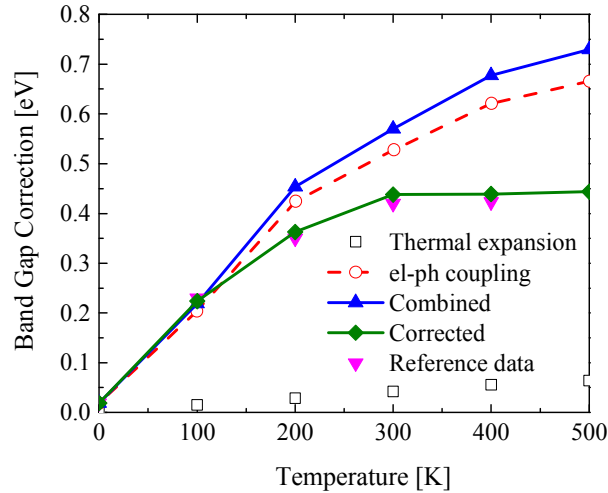


Figure S3. Temperature-dependent band gap of cubic CsPbI₃ perovskite calculated using thermal expansion only (black open square), electron-phonon coupling only within the AHC theory (red dashed-open-circle line), the combined result (thermal expansion + electron-phonon coupling, blue solid-up-triangle line) and the final result corrected with energy scissor (green solid-diamond line) in comparison with the data from ref 15 (pink down triangle).

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