

Dynamic Disorder and Potential Fluctuation in Two-Dimensional Perovskite

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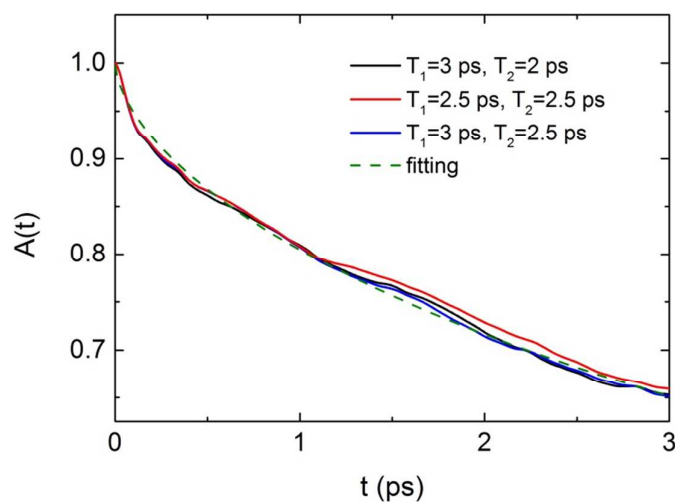


Figure S1. The autocorrelation function $A(t)$ for $t=0-3$ ps. T_1 is the time used for the system to reach equilibration state and T_2 is the time used for the statistics of $A(t)$. Different T_1 and T_2 are tested, and we have used $T_1=3$ ps and $T_2=2.5$ ps for final calculation. It is found that, the autocorrelation function can be fitted by a stretched exponential decay function $A(t) = e^{-0.22t^{0.62}}$. The correlation function decays to 0.66 at $t=3$ ps, and (according to the fitted function) to 0.4 at $t=10$ ps.

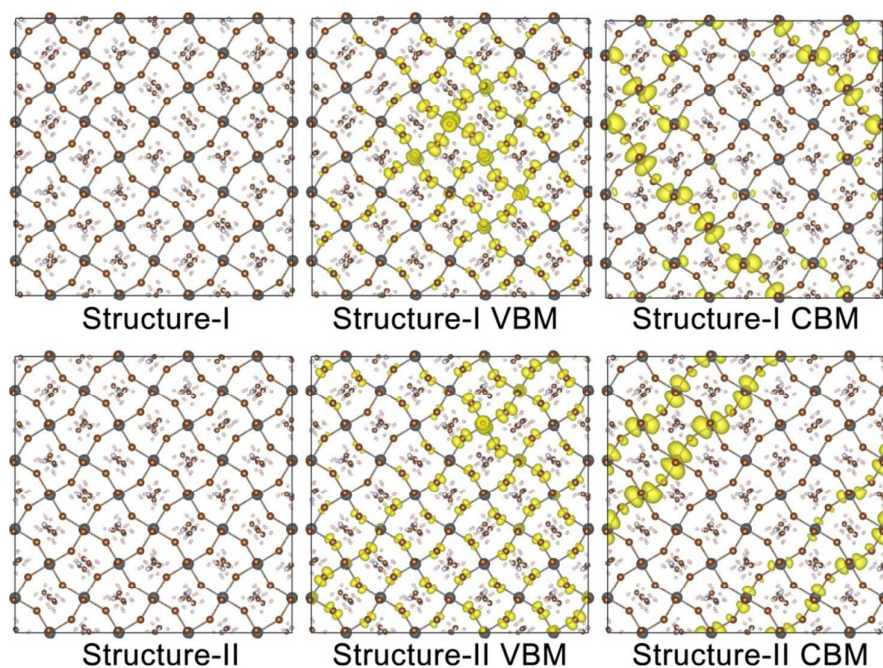


Figure S2. The VBM and CBM of two structures I and II. Structure-I and structure-II have the same PbBr_4 framework, but with different $\text{C}_4\text{H}_9\text{NH}_3$ orientations (thus their charge centers). Despite the same PbBr_4 configuration, the CBM and VBM of the two structures are quite different. According to this analysis, the position of charge centers is indeed important in determining the band edge state characters.

Discussion on the choice of PBE and the empirical correction scheme of Grimme

The main disadvantage of PBE is that it underestimates the band gap. However, in the present work, the band gap value is not the main topic of interest since we do not introduce any deep in-gap state in the system. As is well known, PBE can already give good structural properties and ground state charge density for solids. For a molecule dynamic simulation, the accuracy of PBE (with vdW corrections) is sufficient to give reasonable inter-atomic interactions. In addition, the coulomb potential fluctuation in the system is determined by the ground state charge density, which can also be well described by PBE. Finally, the computational cost of PBE is cheap, allowing large supercell calculations (in the present work there are over 1000 atoms in the supercell). Although other methods like HSE [S1] can give more accurate electronic structure, they can be much more time consuming and thus impractical. In consideration of the balance between accuracy and cost, PBE is an acceptable choice for the present work. It is also widely used by many other works investigating perovskites.

As for the vdW correction, indeed, there are now many (perhaps too many) different approaches to deal with the important vdW interactions, choosing any one method could be accused of ignoring all the others. The reason for us to choose the simple empirical Grimme correction is based on: (1) the efficiency of the method; (2) the availability of it in the code we used; (3) mostly importantly, the accuracy and the robustness of the method. We are doing MD simulation for systems with >1000 atoms with vacuum, thus efficiency is a major concern. Relatively speaking, the simple Grimme's method is still the fastest and is implemented in VASP. As for whether Grimme's method is good enough, we refer to a recent careful comparison by L. Goerigk [S2]. That work systematically compared several vdW functional, including vdW-NL (nonlocal expression) and the vdW-D (Grimme's method). Although in general vdW-NL is found to be the best, the vdW-D just follows closely, and in some cases vdW-D performs even better. The conclusion of Ref. S2 is that both vdW-NL and vdW-D are readily applicable to a large range of chemical elements, and are recommended for general applications. In this sense, the vdW-D method serves as a computationally less demanding option for describing vdW interaction, which is useful in large scale molecular dynamics simulations and similar applications. Besides, due to the simplicity of the vdW-D method, it is computationally most robust.

References

- S1. Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, *118*, 8207–8215.
- S2. Goerigk, L. How Do DFT-DCP, DFT-NL, and DFT-D3 Compare for the Description of London-Dispersion Effects in Conformers and General Thermochemistry? *J. Chem. Theory Comput.* **2014**, *10*, 968–980.