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Dynamic Disorder and Potential Fluctuation in Two-Dimensional Perovskite

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Abstract

The structural and electronic properties of 2D perovskite $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ are investigated from first-principles calculations. It is found that despite the existence of carbon chain, the organic molecule $\text{C}_4\text{H}_9\text{NH}_3$ in 2D perovskite is able to rotate at room temperature, showing a highly dynamic behavior. The dynamic disorder of $\text{C}_4\text{H}_9\text{NH}_3$ introduces dynamic potential fluctuation, which is sufficient to localize the wavefunction and to separate the valence band maximum and conduction band minimum states. We further showed that, rather than a pure dipole rotation model, the disorder effect of the molecules can be better described by the motion of the net charge centers of the molecules, which contributes to the potential fluctuation. Hence, polar molecule is not the necessary condition to create potential fluctuation in perovskite, which is further demonstrated by the calculations of 2D inorganic perovskite Cs_2PbBr_4 .

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The successful isolation of graphene in 2004 has stimulated the field of two-dimensional (2D) atomically thin crystal structures.¹ With the advances in material synthesis in the past decade, a lot of new members have joined the 2D material family.^{2,3} In particular, 2D semiconductors are extremely promising for next-generation ultrathin optoelectronic devices due to their extraordinary properties with reduced dimension, such as strong quantum confinement, enhanced exciton binding, mechanical flexibility, and optical transparency. Since 2009, hybrid organic-inorganic perovskite (HOIP) materials have been emerging as the rising

star in optoelectronic applications, such as solar cells,^{4,5} light-emitting devices,^{6,7} and photo-detectors.^{8,9} HOIPs exhibit many excellent properties like high absorption coefficient,¹⁰ long carrier diffusion length,¹¹ high quantum yield,¹² defect tolerance,¹³ etc. Given the fact that many unique features can appear in materials with reduced dimension, it is thus intriguing to explore the properties in 2D HOIPs. Recently, 2D HOIPs with thickness down to monolayer were successfully synthesized.^{14–18} These 2D HOIPs have the stoichiometry of A_2BX_4 , where A is an long-chain organic molecule such as $C_4H_9NH_3$, B is a metal cation, and X is a halide. Due to the protection of the organic ligand molecules, the stability of 2D HOIP is much improved compared with their 3D counterparts.^{19,20} This solves a major problem in HOIP, namely its poor stability in ambient air, thus might have removed the obstacle for its application. In addition, rich optoelectronic properties have been observed in 2D HOIPs. For example, Dou et. al. showed that $(C_4H_9NH_3)_2PbBr_4$ exhibits purple-blue light emission.¹⁴ Both a high photoresponsivity and extremely low dark current are also achieved in this material.¹⁷ Moreover, several works showed that $(C_4H_9NH_3)_2PbI_4$ has strong exciton effect.^{16,21} These experimental achievements also stimulated theoretical studies focusing on the band structures,^{22,23} defect properties,²⁴ and polaronic effects²⁵ of 2D HOIPs.

Despite of the progress already made on 2D HOIPs, there are still many fundamental questions worth studying. One problem is the dynamics of the organic molecules in 2D HOIPs, and its consequence on the electronic properties. A recent femtosecond transient absorption spectroscopy study suggests the existence of localized states resulted from potential fluctuation in 2D perovskite.²⁶ But there is no direct evidence for this localization. In 3D HOIPs like $CH_3NH_3PbI_3$, it is known that the small CH_3NH_3 molecules show fast rotation^{27–31} and can induce potential fluctuation and wavefunction localization.^{32,33} However, the size of the organic molecules in 2D HOIPs is much larger compared with CH_3NH_3 due to the long carbon chain, resulting in higher energy barrier for rotation. Therefore, it is unclear that whether the organic molecules in 2D HOIPs show dynamic disorder or not, and whether the possible disorder can lead to wavefunction localization. Besides, how the molecules af-

fect the electrostatic potential is also an interesting topic. Previously, the effect of organic molecules in HOIPs is understood by viewing the polar molecules as pure dipoles.^{32,34} However, the organic molecule is in a +1 charged state in HOIPs. Therefore a pure dipole with zero net charge might not be the best description of the system, especially given the fact that local polar fluctuation is also observed in inorganic CsPbBr₃ with non-polar cations.³⁵

In this work, we investigate the structural and electronic properties of 2D perovskite (C₄H₉NH₃)₂PbBr₄ monolayer from first-principles calculations. We find that the C₄H₉NH₃ molecule is highly dynamic, and can induce potential fluctuation and wavefunction localization. We further show that the disorder effect of the molecules can be described by the movement of a net charge centered at the N atom, which has contribution from both rotation and translation.

All the calculations are carried out using the Vienna *ab initio* simulation package (VASP).³⁶ The frozen-core projector augmented wave method³⁷ and the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE)³⁸ is adopted. The wavefunctions are expanded by plane-wave basis sets with a cutoff of 400 eV. For unitcell calculations (ground state structure relaxation and band structure calculation), Brillouin zone is sampled by a $3 \times 3 \times 1$ Monkhorst-Pack special k-point mesh,³⁹ and for supercell calculations (rotation barrier and molecular dynamic simulations) the Γ -point is used. The vacuum layer is larger than 12 Å between two adjacent periodic layers. The convergence threshold for structure relaxation is 0.02 eV/Å. Van der Waals interactions are included by using the empirical correction scheme of Grimme.⁴⁰ Although there are many methods^{41–44} other than the current PBE+Grimme method that could provide slightly better description of the van der Waals interaction, the PBE+Grimme offers the most robust and efficient option for our molecular dynamics simulations. According to a recent work,⁴⁵ the PBE+Grimme is only slightly inferior compared to the nonlocal charge expression of the dispersion energy (See more discussions in the supporting information). Charge population is determined by the Bader charge analysis.⁴⁶ For molecular dynamic simulations a 250 eV cutoff is used to reduce the

computational cost. We have used a large 4×4 supercell, which contains 1248 atoms in total. Ref.³¹ showed that for bulk perovskite, supercells larger than $2\times 2\times 2$ should be sufficient to remove the artificial constraint in the dynamics due to periodic boundary condition. Therefore, the 4×4 supercell used in the present work is appropriate. A canonical ensemble with the Nose thermostat⁴⁷ under 300 K is employed and the time step is 1 fs.

The structure of the 2D $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ is shown in Figure (1)a. The PbBr_6 octahedra adopt an in-plane corner-sharing structure, forming a 2D framework of PbBr_4 . The surfaces of the 2D layer are covered by $\text{C}_4\text{H}_9\text{NH}_3$ cations, with the $-\text{CH}_2\text{NH}_3$ groups located inside the cavities formed by neighboring octahedra, thus the total charge is balanced. The band structure of 2D $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ is shown in Figure (1)b. It has a direct band gap at the Γ point, and the band edge states are well decoupled from the HOMO and LUMO of the $\text{C}_4\text{H}_9\text{NH}_3$ molecule. The VBM mainly consists of Pb s and Br p orbitals, and CBM comes from Pb p orbitals. This is similar to the case of bulk HOIPs.¹³

Figure 1: (a) Top-view (left) and side-view (right) of the structure of 2D perovskite $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$. The dashed lines indicate a unitcell. The pink, dark and blue balls represent I, Pb and N atoms, respectively. (b) PBE calculated band structure of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$, as well as the charge density for CBM and VBM states.

It is well known that the organic molecules in bulk HOIPs are highly dynamic and show

fast rotation, with a relaxation time of a few picoseconds at room temperature.²⁷⁻³¹ The lack of chemical bond between the molecules and the inorganic framework, together with the relatively large cage structure of the framework, results in low rotation barriers⁴⁸ and facilitates the molecular rotations. In 2D $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$, the binding between $\text{C}_4\text{H}_9\text{NH}_3$ and PbBr_4 framework is also non-covalent, and there is plenty of empty space surrounding the $-\text{CH}_2\text{NH}_3$ group. So one may expect that the $\text{C}_4\text{H}_9\text{NH}_3$ molecule is also capable of rotation. As seen in Figure (2)a, the orientation of the N-C axis of the $\text{C}_4\text{H}_9\text{NH}_3$ molecule can be represented by the rotation within the sheet plane (azimuthal angle φ) and the tilt with respect to sheet normal (the polar angle θ). To explore the possibility of molecule rotation, we first constructed a 2×2 supercell of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ and calculated the rotation energy barrier. As a rough estimation, at this step we only consider φ rotation. We choose one of the $\text{C}_4\text{H}_9\text{NH}_3$ molecules and rotate it by $\Delta\varphi$ while relaxing all the other atoms. We consider $\Delta\varphi$ from 0 to 2π , and the barrier of the whole rotation process is calculated by the climbing-image nudged elastic band method,⁴⁹ and the results are shown in Figure (2)b. When $\Delta\varphi$ varies from 0 to 2π , the maximum energy barrier is about 0.32 eV. This value is larger than the rotation barrier of CH_3NH_3 in bulk HOIPs (in the order of 0.1 eV),⁴⁸ nevertheless it is still a low barrier and allows the rotation of $\text{C}_4\text{H}_9\text{NH}_3$. Moreover, the calculated 0.32 eV is just the upper limit of the barrier since only φ rotation is considered. The actual $\text{C}_4\text{H}_9\text{NH}_3$ rotation can adopt other pathways involving θ rotation and other coordination movements.

To gain a better description of the molecule rotation, we did a molecular dynamic (MD) simulation at 300 K in a 4×4 supercell of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ containing 64 $\text{C}_4\text{H}_9\text{NH}_3$ molecules. In Figure (2)c, the coordinates $(\varphi(t), \theta(t))$ of the N-C axis of all the molecules in the supercell are presented over a simulation time of 3.4 ps. It is clearly seen that the molecules show significant rotation in both φ and θ . In this not-so-long trajectory, we are able to see φ reorientation over 180° and θ reorientation over 70° . It'll be interesting to know what's the time scale of the rotation, and whether there is orientation correlation between different molecules. Here we focus on the φ relaxation and correlation since it determines

Figure 2: (a) The polar coordinates (φ, θ) to describe the orientation of the N-C bond of $C_4H_9NH_3$. (b) The φ rotation energy barrier of a $C_4H_9NH_3$ for $\Delta\varphi$ from 0 to 2π . (c) Coordinates $(\varphi(t), \theta(t))$ of the N-C axis for different $C_4H_9NH_3$ molecules over the 3.4 ps MD trajectory. Each color represents one $C_4H_9NH_3$, and there are 64 $C_4H_9NH_3$ in total. The open circles indicate the initial coordinates at equilibrium structure.

the orientation of the N-C axis projection on the sheet plane. The following auto-correlation function can be used to describe the φ relaxation:

$$A(t) = \left\langle \frac{1}{N} \sum_{i=1, N} \hat{n}_i(t + t_0) \cdot \hat{n}_i(t_0) \right\rangle \quad (1)$$

where N is the number of molecules, and $\hat{n}(t) = (\cos\varphi(t), \sin\varphi(t))$ is the unit vector of the N-C axis projection on the sheet plane. The angle brackets stands for time average over different t_0 . If the molecule stays within on local minimum position in Figure (2)c, $A(t)$ for long time t will have a finite number. However, for a activated hopping, $A(t)$ will have a decay behavior. In our calculation, we obtained $A(t)$ using a 8.5-ps MD trajectory (See supporting information Figure (S1)). We find $A(t)$ can be described by a stretched exponential decay function. It decays to 0.66 at $t=3$ ps, and (according to fitted function) to 0.4 at $t=10$ ps. Thus the relaxation time of the molecule rotation should be larger than 10 ps. A rough estimation of the rotation time scale may be several tens of picoseconds. Compared with the CH_3NH_3 molecule whose relaxation time is a few picoseconds, the rotation of $C_4H_9NH_3$

is probably a order of magnitude slower, which is consistent with the above energy barrier estimation. Therefore, the carbon chain in $\text{C}_4\text{H}_9\text{NH}_3$ tends to prevent its rotation. We also expect that the longer is the ligand chain, the slower is the rotation. In case of multilayers, the $-\text{CH}_3$ ends of the $\text{C}_4\text{H}_9\text{NH}_3$ molecules are in contact with each other from the opposite layers. They are not completely free and can have weak interactions, which may make the rotation slightly more difficult. Next, we investigate the dynamical correlation between $\text{C}_4\text{H}_9\text{NH}_3$ molecules. To do this, we calculated the square Pearson correlation coefficient r_{ij}^2 of the $\varphi(t)$ trajectories of neighboring molecules:³¹

$$r_{ij}^2 = \frac{\{\sum_t [\varphi_i(t) - \bar{\varphi}_i][\varphi_j(t) - \bar{\varphi}_j]\}^2}{\sum_t [\varphi_i(t) - \bar{\varphi}_i]^2 \sum_t [\varphi_j(t) - \bar{\varphi}_j]^2} \quad (2)$$

Here $\bar{\varphi}$ is the mean of $\varphi(t)$, and i and j are index of molecules. r_{ij}^2 is an estimation of the fraction of the two variances showing linear correlation. A zero value of r_{ij}^2 indicates two independent variances. The calculated average r_{ij}^2 over all neighboring (i, j) pairs on the 8.5-ps trajectory is 10%. Therefore, the $\text{C}_4\text{H}_9\text{NH}_3$ molecules show some small orientation correlation. Moreover, the calculated $\varphi\varphi$ correlation strength in 2D perovskite here is slightly larger than that in 3D HOIP, which is reported to be around 6% at 300 K.³¹

The above results indicate that the $\text{C}_4\text{H}_9\text{NH}_3$ molecules in 2D perovskite is indeed able to rotate, resulting in a dynamic disorder. Although the $\text{C}_4\text{H}_9\text{NH}_3$ molecules are not directly involved in the band edge states, they create a local electric field and their dynamic disorder can lead to a potential fluctuation, which will influence the properties of the band edge states. Such a effect can be particularly significant for 2D perovskite since in principle, wavefunction localization in a 2D system due to potential perturbation is more likely than in a 3D system. Figures (3)a-(3)c shows the VBM and CBM charge densities for three snapshots ($t=1.6$ ps, 2.2 ps, and 3.2 ps) in the MD trajectory. It is seen that all the VBM and CBM states are strongly localized, and the localization patterns are dynamic and differ at different time. Moreover, there is a spatial separation between VBM and CBM. We also calculated the potential fluctuation $\Delta V = V(\mathbf{r}) - \bar{V}$ for the three structures, as shown

Figure 3: (a)-(c) The charge density of VBM and CBM, and the potential fluctuation ΔV for three snapshots in the MD trajectory. (a) $t=1.6$ ps. (b) $t=2.2$ ps. (c) $t=3.2$ ps. (d)-(f) The same as (a)-(c) but for the NH_4 -based structures. These structures are constructed by changing the $\text{C}_4\text{H}_9\text{NH}_3$ in (a)-(c) into NH_4 . The position of the N atom of the NH_4 is the same as that of the $\text{C}_4\text{H}_9\text{NH}_3$ in the original $\text{C}_4\text{H}_9\text{NH}_3$ -based structure. The PbBr_4 frameworks are not changed.

at the bottom of Figures (3)a-(3)c. Here $V(\mathbf{r})$ is the electrostatic potential at the Pb site and $\bar{V}$ is its average. The root-mean-square of ΔV is 0.2-0.3 eV, i.e., the average potential difference between the high-potential and low-potential regions can be 0.4-0.6 eV. Such a potential fluctuation could be sufficient to cause notable separation and localization of CBM and VBM, overcoming the exciton formation caused by their Coulomb attraction. As shown in Figures (3)a-(3)c, the CBM states are distributed in the low-potential regions, whereas the VBM states are distributed in the high-potential regions. The charge separation can have many impacts to the excitonic and carrier-transport properties of 2D perovskite, such as dissociation of excitons, reduced carrier recombination rates, and long carrier life time. For photovoltaic applications, such an effect can facilitate the separation of photo-generated electrons and holes, and thus can help to improve the performance. However, this CBM and VBM separation can also reduce the radiative recombination between electrons and holes, which decreases the performance of light-emitting devices. Note a recently reported transient

absorption measurement on 2D perovskite suggested the existence of dynamically disordered energy landscape and carrier localization in this system.²⁶ Although it is quite difficult to directly compare the present ground state electronic state calculations with the photo-excited processes in Ref.,²⁶ our result is consistent with the experimental hypothesis, which can be an indirect evidence of the possible existence of localized states in 2D perovskite. Further study on this topic would be very interesting.

We next analyze the dipole effect of the $\text{C}_4\text{H}_9\text{NH}_3$ molecules. In previous studies on bulk HOIPs, the effect of an organic molecule is modeled by a pure dipole moment,^{32,33} and the reorientation of molecule changes the dipole orientation and causes potential fluctuation. However, the organic molecules in perovskite structures have +1 net charge, so they may not be well described solely by a pure dipole with zero net charge. Moreover, there is also no unique definition of the dipole moment for a charged system. Here we provide an alternative view on the effect of the organic molecules. The Coulomb potential $U(\mathbf{r})$ created by a system with charge Q_i at position $\mathbf{R}_i$ can be approximated by the multipole expansion around a point $\mathbf{R}_0$:

$$\begin{aligned} U(\mathbf{r}) &= \sum_i \frac{Q_i}{|\mathbf{r} - \mathbf{R}_i|} \\ &= \frac{Q}{|\mathbf{r} - \mathbf{R}_0|} + \frac{\mathbf{p} \cdot (\mathbf{r} - \mathbf{R}_0)}{|\mathbf{r} - \mathbf{R}_0|^3} + O\left(\frac{1}{|\mathbf{r} - \mathbf{R}_0|^2}\right) \\ &\approx \frac{Q}{|\mathbf{r} - \mathbf{R}_0|} + \frac{\mathbf{p} \cdot (\mathbf{r} - \mathbf{R}_0)}{|\mathbf{r} - \mathbf{R}_0|^3} \end{aligned} \quad (3)$$

Here $Q = \sum_i Q_i$ is the net charge of the system and $\mathbf{p} = \sum_i Q_i(\mathbf{R}_i - \mathbf{R}_0)$ is the effective dipole. If one choose the expansion center $\mathbf{R}_0$ to be the same as the net charge center $\sum_i Q_i \mathbf{R}_i / Q$, then the effective dipole $\mathbf{p}$ becomes zero, and the whole system can be approximated by a point charge Q at $\mathbf{R}_0$ (namely Eq. (3) can be further written as: $U(\mathbf{r}) \approx Q/|\mathbf{r} - \mathbf{R}_0|$ in case that $|\mathbf{r} - \mathbf{R}_0|$ is sufficiently large so higher order terms can be neglected). Using the Bader charge analysis, we found that the net charge center $\mathbf{R}_0$ of the $-\text{CH}_2\text{NH}_3$ group in a $\text{C}_4\text{H}_9\text{NH}_3^+$ cation is located very close to the N atom, with a distance

of only 0.17 Å. Therefore, the Coulomb potential from $\text{C}_4\text{H}_9\text{NH}_3^+$ can be approximated by a point charge at the N site. (This conclusion also holds for CH_3NH_3 as the calculated net charge center is only 0.4 Å away from the N atom.)

To further confirm this, we took the structures of the three snapshots in Figures (3)a-(3)c, and replaced the $\text{C}_4\text{H}_9\text{NH}_3$ molecules by NH_4 molecules which have no intrinsic dipole and act as a point charge. The PbBr_4 frameworks of the original structures in Figures (3)a-(3)c are kept the same, and the NH_4 molecules were put at the N atom sites, which is close to the net charge centers, in the original $\text{C}_4\text{H}_9\text{NH}_3$ -based structures. According to the above analysis, the so-constructed NH_4 -based structures should be analogy to the $\text{C}_4\text{H}_9\text{NH}_3$ -based structures (we expect similar net charge on NH_4 and $\text{C}_4\text{H}_9\text{NH}_3$). The calculated VBM, CBM, and ΔV for the NH_4 -based structures are shown in Figures (3)d-(3)f. As expected, all the results are very similar to those of the original $\text{C}_4\text{H}_9\text{NH}_3$ -based structures in Figures (3)a-(3)c, despite that NH_4 is non-polar whereas $\text{C}_4\text{H}_9\text{NH}_3$ is polar. To verify that the similarity between Figures (3)a-(3)c and Figures (3)d-(3)f is not resulted from the same Pb-Br frame, we did test calculations on two structures with the same Pb-Br frame but different $\text{C}_4\text{H}_9\text{NH}_3$ orientation (thus different positions of charge centers). It is found that these two structures have different CBM and VBM distribution (see supporting information Figure (S2)), indicating that the position of charge centers is indeed critical. The fact that CBM and VBM tends to localized in opposite locations (see Figure(3)) also supports the view of electrostatic potential caused localization. Therefore, the potential fluctuation ΔV can be best viewed as the effect of a point net charge centered at $\mathbf{R}_0$ of the molecule. Thus the biggest effect of the molecule rotation is not to change the orientation of its neutral molecule dipole moment, instead it is to change the position of its charge center $\mathbf{R}_0$. The effects of the displacement of $\mathbf{R}_0$ can still be described by a dipole moment $q\Delta\mathbf{d}$, here $q=1$ is the net charge and $\Delta\mathbf{d}$ is the charge center displacement. However, $\Delta\mathbf{d}$ is not only caused by the molecule orientation change, it can also be produced by a molecule displacement. Besides, the $q\Delta\mathbf{d}$ caused by a molecule flipping is larger than the neutral molecule dipole moment. All

these point out that, a molecule with a dipole moment in neutral state is not the necessary condition to create potential fluctuation and wavefunction localization. As a demonstration of this point, we did a MD simulation on all-inorganic 2D perovskite Cs_2PbBr_4 which is also experimentally synthesized,⁵⁰ and take a snapshot at $t=4.5$ ps as shown in Figure (4). Without the polar molecule, potential fluctuation and wavefunction localization also occur in 2D Cs_2PbBr_4 due to the motion of Cs^+ . Cs^+ ion is in a charged state. As Cs^+ moves within the A-site of the perovskite, it will also cause an effective change of its dipole moment $q\Delta\mathbf{d}$; hence will cause potential fluctuation as the case of $\text{C}_4\text{H}_9\text{NH}_3$ molecule. However, the frequency of the Cs^+ oscillation and its displacement amplitude will be different from that of $\text{C}_4\text{H}_9\text{NH}_3$ molecule. Note this analysis is not limited to 2D perovskite but also applicable to 3D perovskite. Recently there has been experimental study showing similar properties of band edge carrier in both hybrid and inorganic perovskites.⁵¹ Evidences of local polar fluctuations in CsPbBr_3 are also reported.³⁵ More studies in the future is needed to fully understand the extent of wavefunction localization and potential fluctuation in Cs based all-inorganic perovskites. There could be some major difference between all-inorganic and hybrid perovskites (e.g., perhaps less potential fluctuations in average in the former). For example, in Figure (4), we notice significant less localization for the CBM state in Cs_2PbBr_4 compared to that of $\text{C}_4\text{H}_9\text{NH}_3$. One also expects much faster dynamics in Cs based systems due to the lack of displacement barrier. This could also change the carrier dynamics significantly.

Figure 4: A snapshot of the charge density of VBM and CBM, and the potential fluctuation ΔV for 2D inorganic perovskite Cs_2PbBr_4 after 4.5 ps MD simulation.

Finally we would like to make a discussion on the generalization of the present work. Although there can be many kinds of organic molecules accommodated in the 2D perovskite,

the majority of these molecules have a structure of $R\text{-NH}_3$ (R is often an alkyl chain). The R ligand is usually far away from the 2D Pb-halide framework, and the most important interaction is thus the local interaction between -NH_3 group and the Pb-halide framework. In the present work, we studied the $\text{C}_4\text{H}_9\text{NH}_3$ molecule, which has the typical $R\text{-NH}_3$ structure. Replacing the $\text{-C}_4\text{H}_9$ ligand by other by other alkyl chains should not significantly affect the interaction at the -NH_3 end, thus the main conclusion of the present work, namely the ability of the molecule to rotate, the corresponding potential fluctuation, and the point charge model, should still be valid for a wide range of 2D perovskite with the structure of $R\text{-NH}_3$.

In summary, we have studied the structural and electronic properties of 2D perovskite $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ from first-principles calculations. It is found that despite the existence of carbon chain, the organic molecule $\text{C}_4\text{H}_9\text{NH}_3$ in 2D perovskite is highly dynamic and can rotate at a time scale with the order of several tens of picoseconds. MD simulations indicate that the dynamic disorder of $\text{C}_4\text{H}_9\text{NH}_3$ introduces dynamic potential fluctuation and subsequent wavefunction localization in 2D perovskite. We showed that the disorder effect of the molecules can be approximated by the motion of the net charge centers of the molecules, and the potential fluctuation is contributed by such charge center movements. Both the rotation and translation of the molecule can contribute to the net charge center movement. Hence, polar molecule is not the necessary condition to create potential fluctuation in perovskite. This is further demonstrated by the calculations on 2D inorganic perovskite Cs_2PbBr_4 .

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Supporting Information Available:

Calculated autocorrelation function $A(t)$, tests on the effects of the PbBr_4 framework, and a discussion on the choice of PBE and the empirical correction scheme of Grimme.

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