The adsorption postures of water on CH$_3$NH$_3$PbI$_3$ surfaces: a first-principles insight

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Abstract. Inorganic organic perovskite solar cells (PSCs) are a kind of solar cells with rapid development in recent years, but their poor environmental stability, such as the water degradation behavior, hinders their commercialization. Here, we have thoroughly studied the adsorption postures of water on CH$_3$NH$_3$PbI$_3$ surfaces. It is found that the adsorption energy of water molecules on perovskite surfaces is [-0.63, -0.59] eV, and with different initial postures, water molecules could eventually be adsorbed above Pb atom in a horizontal structure. The interaction between the perovskite surface and water molecules mainly comes from the electron exchange of Pb-O atoms. The weak interaction between H-I atoms makes the H atom approach the I atom, which could help maintain a horizontal structure of water molecules. The interactions between perovskite surfaces and water are well explained by our DFT calculations.

1. Introduction

Inorganic-organic perovskite solar cells (PSCs) have attracted extensive attention in the past few years. It has the advantages of high power conversion efficiencies (PCEs), large carrier mobility, long electron hole diffusion, easy preparation and low cost, and can be coated on flexible materials[1]. In the first time, Miyasaka et al. have introduced PSCs in 2009 and the PCE was 3.8%[2]. After the efforts of many researchers, the efficiency of PSCs has improved rapidly, and the latest PCE has exceeded 25%[3]. However, the PSC has a fatal defect that hinders its commercialization, that is its environmental instability.

Many researchers have a consensus that water molecules play a significant role in the decomposition of perovskites. Niu et.al have observed that CH$_3$NH$_3$PbI$_3$ is delicate to dampness [4]. Zhou et al. have indicated that during the preparation of PCEs, controlling ambient humidity (RH ≈ 30%) could increase the PCE to 19.3%[4]. Burschka et al. have showed that in order to obtain high efficiency PSCs, the ambient humidity should be less than 1%[6]. Noh et al. have found that after PSCs were exposed to 55% humidity, the perovskite layer degraded seriously and the PCE of the cells decreased significantly[7]. Also, Frost et al. have noticed that trace water could lead to the partial decomposition of mixed perovskite[8]. These results show that water has a complex effect on the decomposition of PSCs.
The first-principles method is also be used to study the effect of water on perovskite decomposition. Zhang et al. have confirmed that the water molecule could be adsorbed on the perovskite surfaces, and there are different adsorption sites on the perovskite surfaces[9]. Jiang et al. have found that the water molecule and oxygen molecule have significant impacts on the stability of X PbI$_3$ (X= MA, FA, Cs)[10]. Diao et al. have showed that perovskite materials are prone to denaturation in high humidity environment[11]. Ouyang et al. have proposed the water molecule and iodine vacancy can reduce the energy levels of oxygen, promote the transfer of electrons from MAPbI$_3$ to oxygen and then causes the surface photo-oxidation[12].

Many researchers use the first-principles method to study the adsorption of water molecules on the perovskite surfaces, but the effects of the initial postures of water molecules on the adsorption have not been considered. Therefore, in this work we will rotate water molecules along three directions and then study the interactions between water and perovskite surfaces. The paper also includes the following parts. Section 2 presents the computational details and the theoretical methods. In Section 3, the different postures of water molecules on the surfaces are presented and the influence of the initial postures of water molecules on the adsorption are analyzed. Section 4 provides a brief summary of the full text.

2. Computational Methods

We employed the Vienna Ab-initio Simulation Package (VASP) for first-principles calculations under the DFT framework[13]. Simultaneously the projector augmented wave method was used to describe the electron-ion interaction[14]. The energy cutoff for the plane wave basis was set to 500 eV in all calculations. In the simulation, an empirical pair-wise corrections proposed by Grimme in terms of DFT+D2 scheme had also been included for more precisely depicting the dispersion interactions in the systems[15]. In the structural optimization of bulk and interface systems, the pseudopotential we used was the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) [16].

![Figure 1. The optimized stable geometry of the CH$_3$NH$_3$PbI$_3$ surface with one water molecule: (a) side and (b) top view (Black: Pb; Purple: I; Blue: N; Gold: C; Pink: H; Red: O).](attachment:figure1.png)

As shown in figure 1 (a), we construct the super unit of the perovskite (001) surface with one water molecule, and vacuuming 20 Å along the non-periodic direction. The CH$_3$NH$_3$PbI$_3$ plate contains 6.5 units and 78 atoms. The atoms at the bottom layer are pinned to simulate the bulk environment. The related $k$-point arrangement is $6\times6\times1$. The calculated parameters of bulk tetragonal CH$_3$NH$_3$PbI$_3$ perovskites are $a=8.69$ and $c=12.80$ Å, which are in good agreement with other researches[21].
3. Results and Discussion

3.1 The influence of the postures of water molecules on the adsorption

As Hao et al. work demonstrated that the water molecule was favorable to locate on the top of Pb atoms[17], we placed one water molecule above Pb atom in the super unit. To address the impact of the initial postures of water molecules on the adsorption, we firstly optimize the adsorption height on the perovskite surface, and obtain that the water molecule is 2.48 Å above the Pb atom, which is consistent with the previous calculation results. Therefore, we set the initial position of the water molecule at the height of 2.48 Å above the Pb atom, as shown in figure 1(a). Then we take the O atom as the origin and rotate the water molecule along three directions. Figure 2(b) gives the initial posture, where the water molecule is placed horizontally above the Pb atom. We label this posture as P11. Next, with the O atom as the origin, the three rotation directions (x, y and z) are marked in figure 2(c). Figure 2(d) is the top view of a water molecular with an initial parallel posture. We gradually rotate the water molecule clockwise along the z axis by 90 degrees each time, and obtain the postures P12, P13 and P14 in turn. These four postures in a horizontal structure are parallel to the perovskite surface. The postures P21, P22, P23 and P24 can be acquired by rotating the water molecule clockwise along the y axis, and the postures P31, P32, P33 and P34 are along the x axis.

![Figure 2](image_url)

Figure 2. The initial posture of water molecule and three rotation directions: (a)The main and (b) top view of the CH$_3$NH$_3$PbI$_3$ surface with an initial parallel posture of a water molecule; (c) three rotation directions of the water molecule; (d)The top view of the water molecular.

Through the operation of rotating the water molecule, we can totally get twelve initial postures. By removing the repeated postures, we finally chose eight different initial postures to study the adsorption of water molecules on the surface of perovskites. The results of the adsorption position and adsorption energy are listed in Table 1. The equation of the adsorption energy ($E_{ad}$) is defined as:

$$E_{ad} = (E_{slab+H_2O} - E_{slab} - E_{H_2O})$$

where $E_{slab+H_2O}$ is the total free energy of the system with one water molecule adsorbed on the surface, and $E_{slab}$ and $E_{H_2O}$ are the total free energies of perovskite surfaces and an isolated water molecule.
Table 1. Initial postures, final adsorption positions and adsorption energies of water molecules.

| initial posture | adsorption energy | repeated posture | final adsorption position |
|-----------------|-------------------|------------------|---------------------------|
| P11             | -0.61             |                  | P11                       |
| P12             | -0.63             |                  | P12                       |
| P13             | -0.63             |                  | P13                       |
| P14             | -0.60             |                  | P14                       |
| P21             |                   | P11              |                           |
| P22             | -0.61             |                  | P11                       |
| P23             |                   | P13              |                           |
| P24             | -0.61             |                  | P11                       |
| P31             |                   | P24              |                           |
| P32             | -0.63             |                  | P12                       |
| P33             |                   | P22              |                           |
| P34             | -0.59             |                  | P14                       |

It can be seen from Table 1 that the initial postures of water molecules could affect their final adsorption positions. However, no matter how it rotates, the final adsorption position of water molecule is one of the postures P11-P14. When a water molecule is adsorbed on the surface of the perovskite, the adsorption energy is $[-0.63, -0.59]$ eV. Water molecules are always adsorbed above the Pb atom in an almost horizontal posture. By comparing the four adsorption positions of P11-P14, we can obtain that their structures are very similar and when the O atom deviates slightly from the top of the Pb atom, the H atom from water could approach the I atom after the ion relaxation simulations. Taking the P32 posture as an example, we check the energy change of the system when the posture of water molecules changes from the vertical structure to the horizontal one during relaxation as shown in figure 3. It clearly demonstrates that the energy of the system decreases by 1.03 eV in the optimization process. The horizontal structure can minimize the total energy of the system, which is favorable for the stability of the water molecule.

![Figure 3](image_url)  
**Figure 3.** Energy change of the system when the posture of water molecules changes from the vertical structure to the horizontal one during relaxation.

### 3.2 The discussion of the electronic structures

Furthermore, the charge density differences at the perovskite surfaces are given to clarify the interactions of perovskite surfaces and water molecules. Figure 4 depicts the charge density differences (Figure 4
(b)) and plane-averaged charge density differences (Figure 4 (a)) for the system of the perovskite surface absorbed by one water molecule. We can clearly observe the strong Pb-O coupling and weak H-I coupling between the perovskite surface and the water molecule. Electrons are favorable to accumulate around O/I atoms (yellow region) and deplete around Pb/H atoms (green region). Thus, it can be confirmed that the water molecule is energetically favorable to be absorbed on the perovskite surface, and the interaction mainly comes from the electron exchange of Pb-O atoms. Besides, the weak interaction between H-I atoms makes the H atom approach the I atom. Therefore, we can expect that when one water molecule is absorbed horizontally above the Pb atoms on the perovskite surface, the whole system could be relatively stable.

![Figure 4](image_url)

Figure 4. Electron transfer at the interface: (a) main views of the 3D charge density differences; (b) plane-averaged charge density differences along the c direction for the system of the perovskite surface absorbed by one water molecule. The yellow area represents the electron increase, and the green area represents the electron decrease.

4. Conclusion

In conclusion, we used the first-principles simulation to study the adsorption position and adsorption energy of water molecules with different initial postures on the tetragonal CH$_3$NH$_3$PbI$_3$ (001) surface. Our calculation results show that when a water molecule is adsorbed on the surface of the perovskite, the adsorption energy is [-0.63, -0.59] eV, and with different initial postures, water molecules could eventually be adsorbed above Pb atom in a horizontal posture. The interaction between the perovskite surface and water molecules mainly comes from the electron exchange of Pb-O atoms. The weak interaction between H-I atoms makes the H atom approach the I atom, which could help maintain a horizontal structure of water molecules. In general, the effect of different initial structures on water adsorption is relatively small. These results allow us to exclude the influence of the initial postures of water molecules during the adsorption processes. On this basis, we will further study the interaction between multiple water molecules and the perovskite surfaces.

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