Theoretical Studies of the Effects of Metal Ions on the Hydrogen Bonding of Potassium Hydrogen Diacetate

Jiang Bian* and Zhida Chen

State Key Laboratory of Rare Earth Materials Chemistry and Applications, Department of Chemistry, Peking University, Beijing 100871, China

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Studies on the proton-transfer potential energy curves for the potassium hydrogen diacetate system with a short asymmetric hydrogen bond (O···O, 2.476 Å) were carried out by means of ab initio molecular orbital theory and density functional theory. The ab initio theory at the MP2/6-31G* level predicts an asymmetric single-well potential energy function with an O−H distance of 0.998 Å. The asymmetric property of the hydrogen bond is ascribed to the asymmetric distribution of a crystal field constructed by neighboring potassium ions. It is found that the static electric field generated by modeling point charges cannot substitute the role of metal ions in the crystal environment. The computation results show that the hydrogen-bond proton in the free dimer $[H(CH_3COO)_2]^-$ would oscillate between the carboxyl and carboxylate groups, since a relatively flat potential well is found for the H bond. In addition, the performance of both the local approximation DFT SVWN method and the DFT B3P86 method with nonlocal correction is tested in this study, and the latter is found to be comparable with the ab initio calculation at the MP2/6-31G* level.

1. Introduction

Proton transfer along hydrogen bonds in biological and chemical systems has received much attention in past years, both theoretically[1−7] and experimentally.[8−12] The real biological molecules, however, are too large to investigate, and so some small hydrogen-bond molecules and ions, such as $H_5O_2^+$,[13,14] acid dimers,[11,12,15] and acid salts[11,16] were often used as model systems.

Acid salts, in particular the acid formates and acid acetates, were commonly used to model the residues of proteins and enzymes. Potassium hydrogen diformate $[KH(HCOO)_2]$ has been known as a pseudosymmetric type acid salt, which has a short near-symmetric hydrogen bond and two chemically-equivalent COO groups.[16,17] However, potassium hydrogen diacetate $[KH(CH_3COO)_2]$ possesses a short asymmetric hydrogen bond and two structure-distinct COO groups and so is referred to as an asymmetric type of acid salt, although the O···H···O distance(2.476 Å) in $KH(CH_3COO)_2$[18] is similar to the 2.437 Å in $KH(HCOO)_2$. The factor leading to the difference in H-bonding properties between them is complex, but it can be expected that the molecular environment plays an important role in monitoring H-bonding nature. Therefore, a study on the hydrogen bond of $KH(CH_3COO)_2$ is helpful for understanding the relationship between H bonding and its environment. To our knowledge, no theoretical study on the hydrogen bond in $KH(CH_3COO)_2$ has been reported yet.

The influence of metal ions on the proton transfer in a hydrogen bond has been the subject of several papers.[19,20] The effects of external ions on proton transfer in the $(H_2O\cdots H\cdots OH_2)^+$ system were described as a Coulombic interaction between a point charge modeling the external ions and the proton by Scheiner et al.[21,22] A crystal field constructed by a self-consistent set of point charges was developed by Gejii et al.[16] However, the point charge model of metal ions is based upon studies of aqueous solution; its validity for other cases, such as the H bonding in crystals, demands further identification. In the present work, the crystal environment is modeled by five potassium ions in the vicinity of the H-bonding dimer (at distances less than 3 Å to oxygen atoms), by which the effect of the crystal field on the proton-transfer energetics could be evaluated. For comparison with the effect of metal ions, a static electric field built by five +1 modeling point charges is also considered in this work.

Since the validity of ab initio molecular orbital (MO) theory has been established in studying H-bonding systems,[16,23] in this work we investigated the H-bonding energetics in $KH(CH_3COO)_2$ by use of the ab initio calculation at the self-consistent-field (SCF) level. Over the past years, the application of density functional theory (DFT) has been increasing,[13, 24] owning to its encouraging prospect in treating macromolecular systems. Therefore, the performance of DFT, in which both local and nonlocal exchange correlation correction functionals were considered, was also tested in this work.

2. Computational Method

Although the bulk crystal of $KH(CH_3COO)_2$ is electrically neutral, the distribution of charges is asymmetric in a unit cell. It is a fact that there are five potassium ions attached to a H-bonded dimer directly. Therefore, the hydrogen bond in this acid salt is located in a highly polarized surrounding. In the present work, the model is chosen to reflect the specific situation in $KH(CH_3COO)_2$.

Experiment shows that the crystal of potassium hydrogen diacetate $KH(CH_3COO)_2$, is constructed by two building blocks, i.e., K^+ and $[H(CH_3COO)_2]^-$ ions. In our calculation, the free $[H(CH_3COO)_2]^-$ dimer and five nearest neighboring potassium ions are modeled according to the X-ray crystal structure,[18] as shown in Figure 1. Six hydrogen atoms attached to carbon are added with the normal bond length (0.950 Å) and the standard carbon sp^3 hybridization. Such a simplification is reasonable, since our interest focuses on the hydrogen bond but not the side groups. The interatomic distances and angles used are listed in Table 1.

For the purpose of comparing the validities of different levels of theoretical methods, both ab initio and DFT calculations are

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* To whom correspondence should be addressed.

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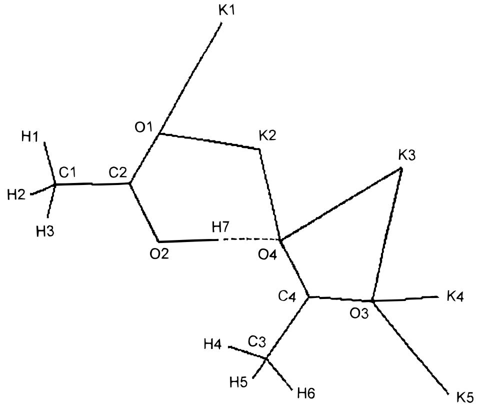

Figure 1. Atomic arrangement of the free $H(CH_3COO)_2^-$ dimer and five neighboring potassium ions (from ref 18). Among the atoms, C1, H1, H2, H3, C2, O1, and O2 correspond to the carboxyl group, while C3, H4, H5, H6, C4, O3, and O4 correspond to the carboxylate group. The structural data are listed in Table 1.

performed by employing the Gaussian 94[25] program package on a HP9000 workstation.

For ab initio MO methods, the second-order Møller−Plesset perturbation (MP2) theory[26] for an electron correlation correction with a 6-31G* basis set and the Hartree−Fock (HF) theory[27] with a 6-31G* basis set are used here.

For the local spin density approximation DFT calculation, the Slater exchange and Vosko−Wilk−Nusair(VWN)[28] local correlation functional are used with a 6-31G* basis set, denoted as SVWN, and for the nonlocal gradient correction DFT, the combination of the Becke three-parameter (B3)[29] gradient-corrected exchange with the Perdew (P86)[30] gradient-corrected correlation is used also with a 6-31G* basis set, denoted as B3P86.

For all computational works, the Los Alamos effective core potential (ECP) operators[31] plus double-ζ set are used for the potassium ions.

In this work, besides the model system in Figure 1, the free dimer $[H(CH_3COO)_2]^-$ and the free dimer in a static electric field with five +1 modeling point charges located in place of the potassium ions are also discussed, by which the role of metal ions in H-bonding systems is evaluated, as shown in the following section.

3. Results and Discussion

The present work is divided into four parts, and the first three sections are results from ab initio methods, i.e., the H-bond potential energy (PE) profiles of the free dimer alone (section 3.1), the free dimer in a modeling static electric field (Section 3.2), and the free dimer in a crystal field (Section 3.3). In section 3.4, the performance of density functional theory is discussed. The PE functions are obtained by calculating the single-point energy of the system for different positions of the H-bond proton H(7), shown in Figures 2−4, where the proton positions are designated by the signs "+"or "−", in which the sign "+" represents a proton position on the side of carboxylate group ($O_3-C_4-O_4$), while the sign "−" indicates a proton position on the side of carboxyl group ($O_1-C_2-O_2$). The parameters of PE curves are listed in Table 2.

3.1. Ab Initio PE Curves for the Free Dimer. The MP2 PE curve, using 6-31G* basis, is shown in Figure 2 by a solid line. An asymmetric broad single well can be seen with a minimum at 0.15 Å, corresponding to an O(4)−H(7) distance of 1.088 Å and having the total energy −456.194 au (1 au = 627.51 kcal/mol). It is worth noting that the energy at −0.15 Å is only 2.17 kcal/mol higher than that at the minimum. Such a shallow well therefore favors the proton oscillating between the carboxyl and the carboxylate groups.

The Hartree−Fock(HF) energy using the 6-31G* basis set is depicted by a dashed line in Figure 2, where a double well with the left minimum (at −0.20 Å) 3.72 kcal/mol higher than the right minimum (at 0.22 Å) can be observed. A barrier with a maximum at −0.03 Å and 4.40 kcal/mol higher than the right well separates the two wells. It is a foregone result since the HF theory has been found to overestimate the proton transfer barrier by some authors.[16] In general, an inclusion of electron correlation correction through, for example, MP2 could improve the potential energy profile. As shown in Figure 2, the MP2 curve using the same basis removes the barrier separating the two minima in the HF curve, and produces a shift of the minimum toward the midpoint of O(2)···O(4).

3.2. Ab Initio PE Curves for the Free Dimer in a Point-Charge-Generated Static Electric Field. The role of alkali metal ion in H-bond systems is often idealized as an electric field generated by point charges with like sign.[21,32] Here we use five +1 point charges to substitute for the potassium ions in the model system (Figure 1), and calculate the H-bond PE curves using ab initio methods in order to understand the role of metal ions in H-bond solids.

These PE profiles in an electric field (in Figure 3) look like those for the free dimer, though some changes are also observed. The minima obtained appear to be insensitive to the addition of point charges. The MP2 PE curve (solid line in Figure 3) has a minimum at 0.16 Å, corresponding to a O(4)···H(7) distance of 1.078 Å, slightly shorter than the value (1.088 Å) for the free dimer. The PE curve at the HF/6-31G* level also has two minima at −0.20 and 0.22 Å, respectively, which agree with their counterparts for the free dimer.

However, the PE curves are distorted by the addition of point charges. For example, the MP2 energy at −0.15 Å is 3.47 kcal/mol higher than the value at the minimum, significantly greater than the energy difference of 2.17 kcal/mol for the free dimer. Greater perturbation of the PE curve at the HF/6-31G* level is observed in the electric field, in which the right minimum differs from the left in energy by up to 4.69 kcal/mol, significantly higher than the corresponding value (3.72 kcal/mol) for the free dimer.

The distortion of the PE curve in the electric field can be attributed to the induced effect of the electric field. Because the point of gravity of the electric field is close to the carboxylate group, more negative charges are drawn from the carboxyl group toward the carboxylate group by the positive point charges. And therefore, the proton H(7) is drawn toward the carboxylate group. As shown in Table 3, the carboxylate group in the electric field has a higher negative charge than that of the free dimer. Thus, the role of the idealized electric field can be described as an indirect induced effect on the proton H(7).

It should be noted here that the Coulombic repulsion of the point charges to H(7) seems being "shielded" off, so that the proton is drawn closer to the electric field.

3.3. Ab Initio PE Curves for the Free Dimer in a Crystal Field. A simplified crystal field is built using five neighboring potassium ions (cf. the model in Figure 1). The PE profiles of the hydrogen bond in the crystal field, computed by ab initio methods at different levels, are shown in Figure 4.

Similarly, narrow single-well PE curves are observed with the minima in the left of midpoint of O(2)···O(4), showing that H(7) is close to the carboxyl group. The MP2 theory yields a single well with a minimum at −0.24 Å, corresponding to a O(2)−H(7) bond length of 0.998 Å, and having a total energy −594.460 au. However, the HF/6-31G* method yields a PE

TABLE 1: Interatomic Distances (in angstroms) and Angles (in degrees) Used in the Present Computations (from Ref 18)[a]

distance		angle		torsion angle	
r(C1−C2)	1.510	a(O1−C2−C1)	122.2		
r(C3−C4)	1.491	a(O2−C2−C1)	114.3	t(O2−C2−C1−O1)	−179.7
r(C2−O1)	1.211	a(H7−O2−C2)	115.6	t(O4−O2−C2−C1)	175.8
r(C2−O2)	1.290	a(C4−O4−H7)	115.0	t(C4−O4−O2−C2)	−175.3
r(C4−O3)	1.247	a(O3−C4−O4)	121.2	t(O3−C4−O4−O2)	173.0
r(C4−O4)	1.268	a(C3−C4−O4)	119.5	t(C3−C4−O4−O2)	−8.6
r(O2···O4)	2.476	a(O4−O2−C2)	115.6	t(H7−O2−C2−C1)	175.8
r(K1−O1)	2.756	a(K1−O3−C2)	140.0	t(K1−O1−C2−C1)	−84.7
r(K2−O4)	2.855	a(K2−O4−O2)	87.4	t(K2−O4−O2−C2)	39.2
r(K2−O3)	2.812	a(K3−O3−C4)	96.8	t(K3−O3−C4−O4)	−28.3
r(K4−O3)	2.714	a(K4−O3−C4)	120.2	t(K4−O3−C4−O4)	71.9
r(K5−O3)	2.771	a(K5−O3−C4)	127.1	t(K5−O3−C4−O4)	−153.4
r(C1−H1)	0.950	a(H1−C1−C2)	109.47	t(H1−C1−C2−O1)	30.1
r(C1−H2)	0.950	a(H2−C1−C2)	109.47	t(H2−C1−C2−O1)	−89.9
r(C1−H3)	0.950	a(H3−C1−C2)	109.47	t(H3−C1−C2−O1)	150.1
r(C3−H4)	0.950	a(H4−C3−C4)	109.47	t(H4−C3−C4−O4)	36.7
r(C3−H5)	0.950	a(H5−C3−C4)	109.47	t(H5−C3−C4−O4)	−83.3
r(C3−H6)	0.950	a(H6−C3−C4)	109.47	t(H6−C3−C4−O4)	156.7

[a] C−H distances are set to 0.950 Å, the H−C−H angles are set according to the standard sp^3 hybridization, and the torsion angles of H−C−C−O are arranged to fit the energy minima.

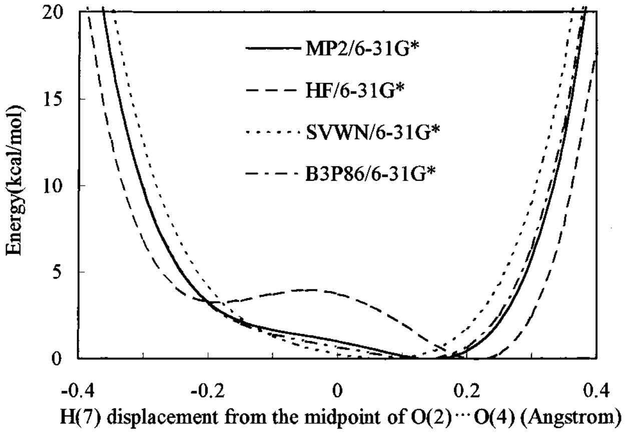

Figure 2. Potential energy profiles for the free H(CH$_3$COO)$_2^-$ dimer as a function of H(7) displacement from the midpoint of O(2)···O(4). The signs of "+" and "−" represent the position of proton H(7) in the side of carboxylate and carboxyl group, respectively. The PE curves are drawn by setting the energies at the minima to zero. The PE minima for MP2/6-31G*, HF/6-31G*, SVWN/6-31G*, and B3P86/6-31G* are situated at 0.15, 0.22, 0.08, and 0.14 Å, respectively.

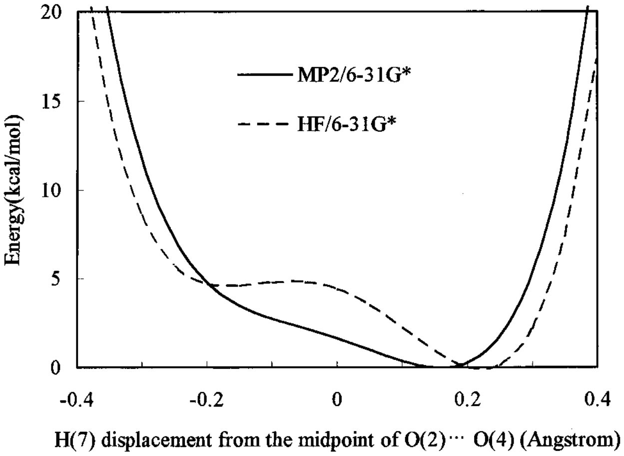

Figure 3. Potential energy profiles for the free H(CH$_3$COO)$_2^-$ dimer in a modeling static electric field generated by point charges as a function of H(7) displacement from the midpoint of O(2)···O(4). The signs of "+" and "−" represent the position of proton H(7) in the side of carboxylate and carboxyl group, respectively. The PE curves are drawn by setting the energies at the minima to zero. The PE minima for MP2/6-31G* and HF/6-31G* are situated at 0.16 and 0.22 Å, respectively.

curve with a minimum at −0.28 Å, corresponding to a shorter O(2)−H(7) bond length (0.958 Å) compared with that from the MP2 method. This result shows that HF theory without electron correlation for this case cannot describe the H-bond energetics correctly.

Under the crystal field, the PE well becomes narrow, which can be due to the neighboring heavy metal ions and, in addition, the increased net charges on the carboxyl and carboxylate groups attached to the hydrogen bond (cf. Table 2). In the previous sections, we have observed that both PE curves of [H(CH$_3$COO)$_2$]$^-$ in the free state and in the electric field are characteristic of a very broad and flat well, and so it favors proton oscillation between the donor and the acceptor. Then, on the contrary, the narrow H-bond well for KH(CH$_3$COO)$_2$ crystal is unfavorable to a proton transfer in the hydrogen bond.

It is interesting to note that, by adding the potassium ions into the model system, the PE minimum shifts from the side of carboxylate group to the side of carboxyl group (Figure 4). This result shows that the metal ions are one of the key factors to maintaining the proton position, and it is of particular interest to investigate the operation mechanics by which the metal ions control the PE profile and even the nature of a hydrogen bond. As known, the metal ions are distinctive from the point charges by having themselves electrons and valence orbitals. Thus, the metal ions can cause charge transfers from methyl groups to COO groups, but the point charges cannot do so. We can find the evidence for such a charge transfer in Table 3. The net charges of both carboxylic and carboxylate groups do increase, and both methyl groups become more positive. In addition to these, the net charges of both the acetic group and acetate group decrease after the intervention of potassium ions, since these metal ions take negative charges from the groups. This result shows that the metal ions affect the H-bonding system through direct Coulombic interaction.

The Coulombic repulsion of the crystal field on H(7) is significant, since H(7) is pushed toward the carboxyl group. Here it is interesting to note that the shielding effect observed in the electric field ceases to be effective in the crystal field. The charge transfers between the metal ions and the oxygen atoms might be responsible for this result.

3.4. DFT PE Curves. In previous parts, we have discussed the calculated results of the H-bond PE curves using ab initio

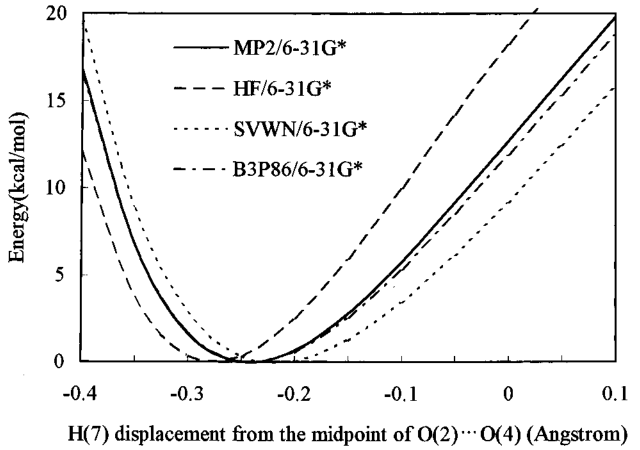

Figure 4. Potential energy profiles for the free $H(CH_3COO)_2^-$ dimer in a crystal field constructed by five neighboring potassium ions, as a function of H(7) displacement from the midpoint of O(2)···O(4). The signs of "+" and "−" represent the position of proton H(7) in the side of carboxylate and carboxyl group, respectively. The PE curves are drawn by setting the energies at the minima to zero. The PE minima for MP2/6-31G*, HF/6-31G*, SVWN/6-31G*, and B3P86/6-31G* are situated at 0.24, 0.28, 0.22, and 0.24 Å, respectively.

TABLE 2: Parameters of Potential Curves for the Hydrogen Bond in $[H(CH_3COO)_2]^-$

model	method	basis set	minima	O(4)···H(7) (Å)	E_{min} (au)
free dimer	MP2	6-31G*	single	1.088	−456.194
	HF	6-31G*	double	1.018	−454.972
	SVWN	6-31G*	single	1.158	−455.194
	B3P86	6-31G*	single	1.098	−458.665
free dimer in EF[b]	MP2	6-31G*	single	1.078	−455.502
	HF	6-31G*	double	1.018	−454.279
in CF[b]	MP2	6-31G*	single	0.998[a]	−594.460
	HF	6-31G*	single	0.958[a]	−593.262
	SVWN	6-31G*	single	1.018[a]	−599.156
	B3P86	6-31G*	single	0.998[a]	−594.893

[a] O(2)···H(7) bond lengths. [b] EF denotes the electric field, and CF denotes the crystal field.

TABLE 3: Atomic and Group Net Charges of $[H(CH_3COO)_2]^-$ at the Minima by MP2/6-31G*

		acetic group		acetate group	
	H(7)	CH_3	CO_2	CH_3	CO_2
free dimer	0.59	−0.05	−0.79	−0.01	−0.73
free dimer in EF[a]	0.59	0.04	−0.76	−0.03	−0.82
free dimer in CF[a]	0.59	0.15	−0.82	0.26	−0.95

[a] EF denotes the electric field, and CF denotes the crystal field.

methods. It is found that the MP2 theory can describe the H-bond energetics in a reasonable way. Here, we examine the performance of both local and nonlocal DFT methods in describing the PE profiles of the hydrogen bond in $KH(CH_3COO)_2$.

As shown in Figure 4, depicted by a dotted line, the PE curve in the crystal field obtained by local DFT/SVWN method is found with a minimum at −0.22 Å, close to the MP2 result (−0.24 Å). But apparently, the local DFT method cannot give a correct PE profile of the free dimer $[H(CH_3COO)_2]^-$. As shown in Figure 2, local DFT/SVWN method predicts a minimum at 0.08 Å, distinct from the MP2 value (0.15 Å).

The nonlocal DFT/B3P86 method using the 6-31G* basis set improves the PE function significantly, compared with that from the local DFT method. The B3P86 minima are observed at 0.14 Å for the free dimer (Figure 2) and at −0.24 Å for the dimer in the crystal field (Figure 4), both of which are very similar to corresponding MP2 results. These results show that the DFT/B3P86 method is a potential useful tool in studying H-bonding systems.

For the free dimer (Figure 2), we found both local and nonlocal DFT methods underestimate the potential energy near the midpoint (−0.1~0.1 Å) of O(2)···O(4) by less than 1 kcal/mol, and the local DFT/SVWN method overestimates the O(4)···H(7) distance by 0.07 Å. This is consistent with the previous finding by other authors.[24] For the free dimer under the crystal field, local and nonlocal DFT functionals yields similar proton sites to the MP2 level.

4. Conclusion

We have carried out ab initio and density functional theory studies on the hydrogen bond in $KH(CH_3COO)_2$. By using the MP2/6-31G* method, we found an asymmetric single-well potential energy function, with a O(2)−H(7) distance of 0.998 Å, for the hydrogen bond in a crystal field constructed by five neighboring potassium ions. It is found that the metal ion is one of the key factors in determining the proton position in a hydrogen bond.

It is also shown in the present work that the modelized electric field generated by point charges with like sign could not substitute for the roles of metal ions, since there are charge transfers between metal ions and oxygen atoms, by which the Coulombic repulsion of the metal ions could penetrate the shield formed by oxygen atoms and push the H-bond proton away.

In the case without the crystal field, a very broad and flat single well is yielded for the free dimer, with a O(4)···(7) distance of 1.088 Å, by a MP2/6-31G* calculation. This result shows that the H-bond proton transfers to the carboxylate group in vacuum, where the proton needs only 2.17 kcal/mol to return to the side of carboxyl group (−0.15 Å). Therefore, in fact, the proton in the hydrogen bond could oscillate between both groups to some extent.

For the free dimer, it is found that HF theory at the 6-31G* level cannot yield accurate results compared to with the MP2 method, because the former generally overestimates the proton-transfer barrier. The local DFT/SVWN methods gives a PE profile without the potential barrier as the MP2 method, but it predicts a too long O(4)···O(7) distance compared to the MP2 value. However, it is found that the nonlocal DFT/B3P86 method gives compatible results with the MP2 value.

For the case of the crystal field, almost all methods give similar O(2)−H(7) bond lengths. It is noted that the nonlocal DFT/B3P86 method yields the same value as MP2, showing a bright perspective for the nonlocal DFT method in studying H-bond systems of larger molecules.

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