Study of electronic structure and dynamics of interacting free radicals influenced by water

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We present a study of electronic structure, stability, and dynamics of interaction and recombination of free radicals such as HO_2 and OH influenced by water. As simple model calculations, we performed *ab initio* and density functional calculations for the interaction of HO_2 and OH in the presence of water cluster. Results indicate that a significant interaction, overcoming the repulsive Columbic barrier, occurs at a separation distance between the radicals of 5.7 Å. This confirms early predictions of the minimum size of molecular dianions stable in the gas phase. It is well known that atomic dianions are unstable in the gas phase but molecular dianions are stable when the size of the molecule is larger than 5.7 Å. *Ab initio* molecular dynamics calculations with Car–Parrinello scheme show that the reaction is very fast and occurs on a time scale of about 1.5 ps. The difference in stability and dynamics of the interacting free radicals on singlet and triplet potential energy surfaces is also discussed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3100549]

I. INTRODUCTION

Free radicals are the most important species in the atmospheric chemistry. Because of the unpaired electrons, free radicals are very reactive and are involved in almost all key reactions occurring in the atmosphere,[1–6] including the formation and depletion of ozone.[7–11] A class of important free radical reactions is between closed-shell molecules and free radicals, with the molecules oxidized due to the strong electron gain ability of free radicals. One common feature of these reactions is the formation of a molecule-radical complex as the reaction precursor. The most oxidative free radicals include OH and HO_2.[12–14] Another type of reaction that free radicals undergo is the recombination reaction leading to close-shell or more stable molecules. For example, two OH radicals can form H_2O_2 molecule. In the atmosphere, many recombination reactions are catalyzed by polar and nonpolar chaperon molecules.[10,11]

Aerosol is one of the most important transportation media of species in the atmosphere. The impact of aerosols on the behavior of the atmospherically important free radicals has been the focus of several studies.[12–25] A polar molecule on an aerosol surface may form hydrogen bond complexes with free radicals. Water molecules in both gas and liquid phases are the main content of the aerosol surface under most conditions since it is in large abundance in the atmosphere and has a high tendency to form hydrogen bonds with free radicals. This also helps increase the accommodation ability of aerosols. On the other hand, the water molecules can also catalyze recombination reactions between free radicals.[10–12] So it is interesting to understand how free radicals interact in the gas phase on an aerosol surface, which can be modeled by water clusters. The interaction between open-shell systems are usually complex because the potential energy surface (PES) of different spin states may exist. An electronic structure study should provide insight on the mixing of atomic orbital and chemical bonding process between free radicals. In this paper, we use quantum chemical methods to study the interaction between the free radicals OH and HO_2. The mixing of wave functions during interaction is also investigated by the natural bond orbital (NBO)[26–30] theory, which will depict the overlapping of the orbital with the reaction. According to the NBO theory, each pair of valence natural hybrid orbitals leads to a complementary pair of valence bonding and antibonding orbitals, and the treatment of bond-antibond interactions constitutes its most unique and characteristic contribution. The NBO analysis can provide direct insight into the interactions that stabilize the hydrogen bonding complexes.

The chemical reaction between free radicals in the atmosphere includes both diffusion and reaction processes. The diffusion of the free radicals is caused by the long-range attractive force between the two open-shell systems originated from the van der Waals interaction. In the reaction process, when the distance between the two free radicals becomes sufficiently short, the wave functions of the two free radicals may mix strongly and the PES of different multiplicity may cross each other. On the surface of an aerosols in the atmosphere, the reaction should also be studied in the presence of water molecules since the water molecules may have strong impact on the reactivity of the species that can have hydrogen bonding interaction with them.[31–34]

It has also been found that electrons can bind to the cluster of water molecules.[35–39] Thus, it is meaningful to investigate the free radical interactions under the condition that H_2O molecules are present. In a system with many free radicals, the interaction between unpaired electrons may cause both electrostatic repulsion and chemical bonding effect. If the system is a multiply charged anion (MCA), the feature can be investigated by examining the Repulsive Coulomb

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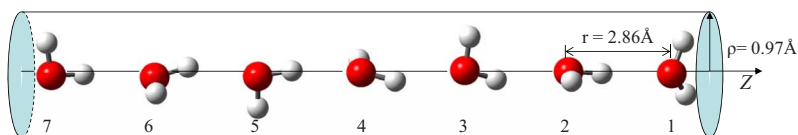a)Author to whom correspondence should be addressed. Electronic mail: francisc@purdue.edu.

FIG. 1. (Color online) The geometry of the linear $(H_2O)_7$ complex optimized at the level of B3LYP/6-31G(d). The O–O distance is fixed at 2.86 Å and the O–H distance is about 0.97 Å.

Barrier (RCB).[40–45] In this work, we employ a linear water cluster as a simple model to investigate electronic structure and dynamics of interacting free radicals influenced by water. From classical electrostatics, the electrostatic potential between an electron ($q=e$) and a dielectric sphere of radius R is given by[44]

$$\varphi(\mathbf{r}) = \frac{q}{|\mathbf{r} - \mathbf{r}'|} - \sum_{l=0}^{\infty} q \frac{(\epsilon - 1)l}{(\epsilon + 1)l + 1} \frac{R^{2l+1}}{r^{l+1} r'^{l+1}} P_l(\cos\theta), \quad (1)$$

where ϵ is the relative dielectric constant, $\mathbf{r}'$ is the position of the electron, and $\mathbf{r}$ is an arbitrary point outside of the sphere, $P_l(\cos\theta)$ is the lth Legendre polynomial and θ is the angle between the vectors $\mathbf{r}'$ and $\mathbf{r}$. In Eq. (1) the first term is the direct Coulomb term from the electron and the terms in the summation correspond to the different polarized fields of the sphere induced by the electron. For spherical molecular dianions, in the first-order approximation and taking the leading term in the summation $l=1$ and $\epsilon=4.4$, it was estimated that the transition from stable to metastable dianions occur when the radius of the spherical molecule is about 5.5 Å.

The long-range interaction between an outgoing electron and the system is dominated by electrostatic repulsion and the short-range interaction is mainly attraction. The combination of long-range and short-range interactions arises a barrier, RCB, on the PES along the reaction or bonding formation path. Dreuw and Cederbaum[41,42] proposed a method to evaluate the RCB potentials using *ab initio* methods. Shi and Kais[46] studied the BeC_4^{2-} dianion with density functional theory (DFT) and found that the crossing point for autodetachment in the linear dianion is 3.25 Å. In their later work, they presented finite size scaling calculations[47] of the critical parameters for binding two electrons to a finite linear dipole field.[48] The two free radical system differs from MCA in that the free radicals are neutral so that the unpaired electrons do not have long-range repulsion. In fact, the recombination of open-shell systems free of this restriction will occur without a barrier. However, on the surface of an aerosol, water molecules may form hydrogen bonds with the free radicals and a pseudobarrier for two free radicals can be assumed.

In the present work, we use *ab initio* and density functional methods to obtain the PESs for the interacting free radicals in the presence of linear water clusters. Then *ab initio* molecular dynamics study are performed to obtain the time scale of interaction and recombination of these free radicals in the presence of water molecules.

II. COMPUTATIONAL METHODS

DFT (Ref. 49) method is adopted in many theoretical investigations on atmospherically important free radicals, molecular clusters, and molecule-free radical complexes.[17–19,50–53] Here, for the quantum chemical calcu-

lations, we use the Unrestricted Becke's three-parameter density functional and the Lee, Yang, and Parr functional to describe gradient-corrected correlation effects (UB3LYP)[54–56] with the 6-31G(d) and the family of augmented correlation-consistent polarized valence basis sets of triple zeta quality (aug-cc-pVTZ).[57,58] The calculations are performed for $(OH)_2(H_2O)_n$ and $(HO_2)_2(H_2O)_n$ systems. The linear water clusters of size ($n=4-7$) is constructed by partial optimization of the PES with geometry constraints on the O atoms in the H_2O molecules. The distance between each pair of O atoms in two adjacent water molecules is fixed at 2.86 Å which is the optimized distance in the water dimer at the level of UB3LYP/6-31G(d) as shown in Fig. 1. (The angle formed by three adjacent O atoms in H_2O molecules is set as 178° instead of 180° for numerical stability). The stable configurations of $(OH)_2(H_2O)_7$ and $(HO_2)_2(H_2O)_7$ systems are also found by partial optimization with the same restriction as the linear water clusters but no constraints are added on the radicals. Since the PES involved in the radical interaction is composed by singlet and triplet PESs in the OH+OH and HO_2+HO_2 systems, the calculations are also performed on these PES separately. The NBO analysis is also used to analyze the bonding features of free radicals. In order to understand the effect of the water molecules on the free radicals and determine whether a barrier exists, the calculations start with the initial guess of optimization by locating the radicals at the two ends of the clusters, position (1,7). For the purpose of investigating the dynamics of the bond formation process in the radical association with the presence of water molecules on aerosol surface at minimum computational cost, the *ab initio* molecular dynamics with the Car–Parrinello scheme (CPMD)[59–62] for the $(OH)_2(H_2O)_4$ system are carried out. In this work, the generalized gradient approximation to DFT of Perdew–Burke–Ernzerhof (PBE96) (Ref. 63) exchange correlation energy is adopted. The CPMD simulation is performed with a time steps of 0.1 fs in an (NVT) ensemble in a 20 Å cubic box with a constant temperature of 298.15 K.[64–66] The DFT and *ab initio* molecular dynamics calculations are performed using the GAUSSIAN03 program suite[67] and the NWCHEM software package.[68]

III. RESULTS AND DISCUSSION

The optimized geometries for the linear $(H_2O)_7$ complex is shown in Fig. 1. The cluster can be treated as a cylinder with a radius of 0.97 Å, which is the bond length of H–O. The molecules from right to left are labeled 1 to 7. The two end water molecules form one hydrogen bond, while the other five water molecules act both as a hydrogen donor and a hydrogen acceptor. Each water molecule has at least one dangling hydrogen atom which facilitates the hydrogen bonding with other species. There may be other possible stationary points on the PES with the same constraints. How-
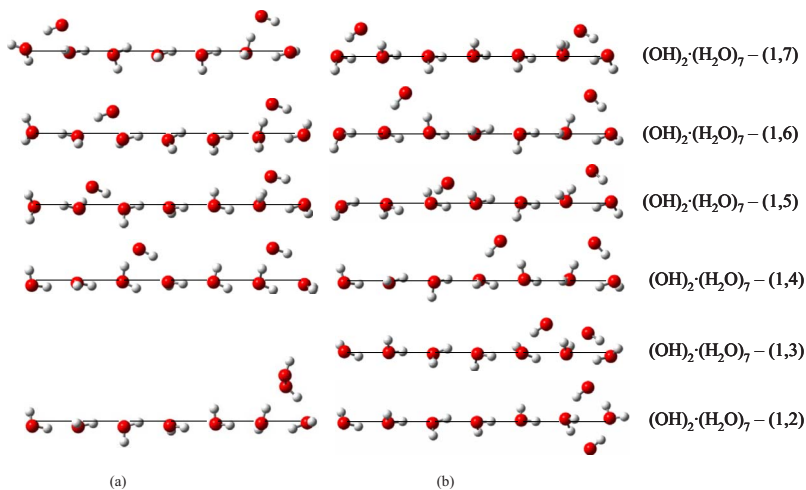
$(OH)_2 \cdot (H_2O)_7 - (1,7)$

$(OH)_2 \cdot (H_2O)_7 - (1,6)$

$(OH)_2 \cdot (H_2O)_7 - (1,5)$

$(OH)_2 \cdot (H_2O)_7 - (1,4)$

$(OH)_2 \cdot (H_2O)_7 - (1,3)$

$(OH)_2 \cdot (H_2O)_7 - (1,2)$

(a)   (b)

FIG. 2. (Color online) The geometries of the interacting OH radicals at different positions with respect to the O atoms in the $(H_2O)_7$. (a) singlet PES and (b) triplet PES.

ever, it has been found that on the surface of water droplets there are dangling H atoms[16,18] available for hydrogen bonding to the free radicals. This means that the adopted linear cluster model is a good approximation of the minimum aerosol surface. Simultaneously, the hydrogen bond sites form potential wells on the PES that prevent them from associating without a barrier.

The $(OH)_2(H_2O)_n$ complexes are shown in Figs. 2(a) and 2(b) for singlet and triplet PESs, respectively. The geometries are optimized from the initial guesses obtained by making one of OH radical hydrogen bond to one of the end

water molecules and the position of the other OH radical varies along the linear chain of water molecules. The purpose of this "movement" is to elucidate the impact of the H_2O molecules on the stationary points of PES along the recombination reaction path of the two OH radicals. As shown in Fig. 2, the OH radicals can be hydrogen bound to two H_2O molecules and their positions are defined by the labels of the corresponding water molecules they form hydrogen bond to as a hydrogen donor. The binding energies (BEs) of the $(OH)_2(H_2O)_7$ system on the two multiplicities are shown in Figs. 3(a) and 3(b). The values are calculated as follows:
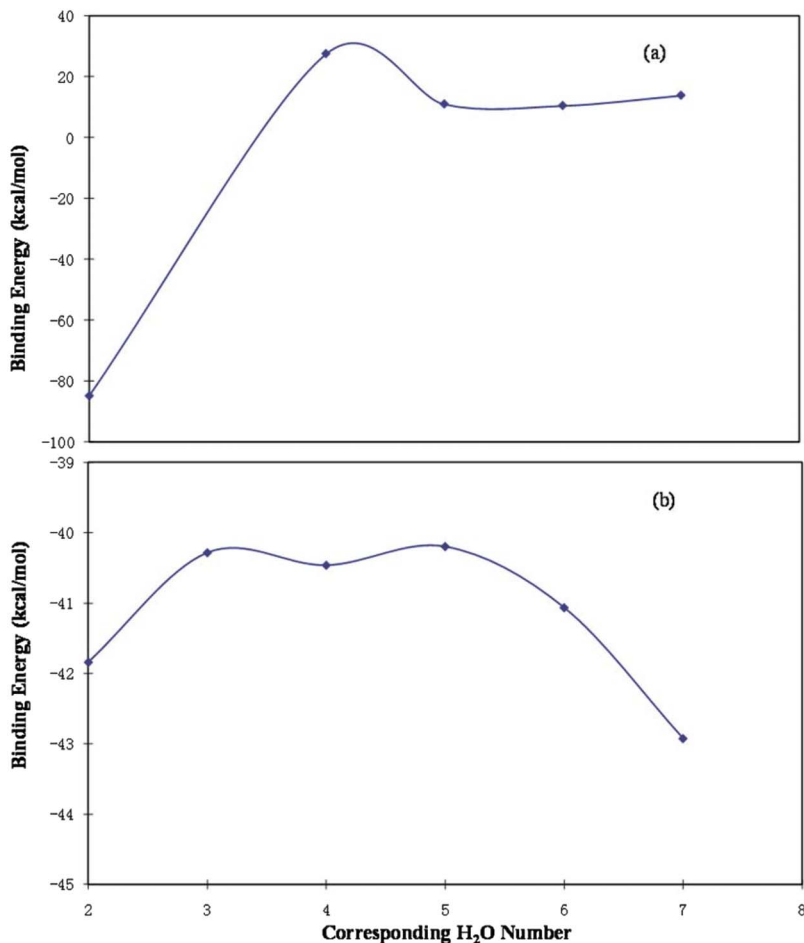

FIG. 3. (Color online) The BE of $(OH)_2(H_2O)_7$ for different positions of the radicals as shown in Fig. 2: (a) singlet PES and (b) triplet PES.
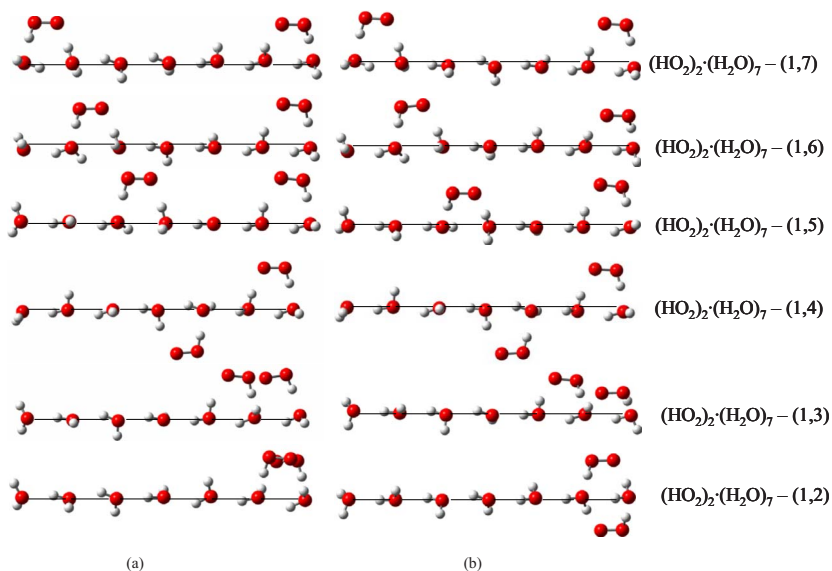
$(HO_2)_2 \cdot (H_2O)_7 - (1,7)$

$(HO_2)_2 \cdot (H_2O)_7 - (1,6)$

$(HO_2)_2 \cdot (H_2O)_7 - (1,5)$

$(HO_2)_2 \cdot (H_2O)_7 - (1,4)$

$(HO_2)_2 \cdot (H_2O)_7 - (1,3)$

$(HO_2)_2 \cdot (H_2O)_7 - (1,2)$

(a)   (b)

FIG. 4. (Color online) The geometries of the interacting HO_2 at different positions with respect to the O atoms in the $(H_2O)_7$: (a) singlet (PES) and (b) triplet PES.

$$BE = E((OH)_2(H_2O)_7) - 2E(OH) - 7E(H_2O).$$

When the OH radicals are in the positions (1,4), (1,5), (1,6), and (1,7), their BEs on the singlet PES are much higher than their corresponding positions on the triplet PES. The (1,4) configuration is about 15 kcal/mol higher than the other three. When the OH radicals are in (1,2) configuration, where a H_2O_2 molecule is formed as shown in Fig. 2(a), a resulting steep potential drop can be seen and the energy is much lower than (1,2) on the triplet PES. The minimum of PES for (1,3) configuration is not found, which indicates that the two free radicals start to have strong electron pairing effect after the two radicals pass the potential well in the (1,4) configuration. The OH radicals start with a (1,3) configuration by the linear minimum search that leads to the potential minimum where the H_2O_2 is formed. The lack of a PES minimum may also suggest that a state crossing occurs at the (1,3) configuration if one compares the singlet and triplet energy curves. Although the optimization cannot indicate the true trajectory of the dynamics of the OH radical, it does suggest that the OH radical will have a strong energetic tendency to recombine to the new molecule H_2O_2 in the singlet PES. In the triplet PES, all the minimum geometries from (1,2) to (1,7) are found as shown in Fig. 2(b). The OH radicals all form hydrogen bonds to neighbor H_2O molecules.

The HO_2 radical is also studied in this work. In the previous work, Francisco et al.[16,18] studied its interaction with cagelike water clusters. It is found from these studies that the HO_2 radical can form stable complexes with water clusters in the atmosphere and that their binding is a localized interaction. In our work, two HO_2 radicals on the linear water cluster surface are investigated. The initial positions of the radicals in the optimization are similar to the case of OH radicals. One of the HO_2 radical is initially located near the end H_2O molecule, and the other radical "moves" on the H_2O molecules labeled from 2 to 7. The labels of HO_2 radicals are set as the labels of the water molecules closest to the two O atoms with the largest distance in the two HO_2 radicals. The minimum geometries of the stable complexes with HO_2 radicals configuration from (1,2) to (1,7) are shown in

Figs. 4(a) and 4(b) for singlet and triplet multiplicities, respectively. The corresponding BEs are shown in Figs. 5(a) and 5(b).

The energy change with the moving HO_2 position with the multiplicity 1, i.e., no unpaired electrons shown here is similar to that of the OH radical. The BE does not change significantly from the (1,4) to (1,7) configurations. When the two radicals are bound to the water molecules labeled (1,2) and (1,3) we can find a significant potential decrease. This is because the singlet PES for HO_2 leads to the reaction producing H_2O_4 molecule and the pairing tendency of the two single electrons is strong. The consistency of OH and HO_2 radicals with singlet multiplicity is a strong suggestion that strong interaction between two free radicals toward formation of the recombination reaction starts with the configuration that the H_2O molecules the two free radicals bound to are direct neighbors or have only one H_2O molecule between, i.e., configuration (1,2) or (1,3). The energy curve on the triplet PES of HO_2 is flat, also as that of OH even though the formation of O_2 and H_2O_2 is possible in the triplet PES. Anglada et al.[69] studied the complexes, transition states, as well as the kinetics of the two HO_2 radicals on both potential surfaces by ab initio calculations. They found that the two HO_2 radicals can form a stable hydrogen bond complex without any reaction. This agrees well with our results. Each point on the plotted energy curve shown in Figs. 3 and 5 is a result of local energy minimization. This means that the traverse from one configuration to another is substantially a process from one potential well to another, and the barrier between them should be determined by the difference between the local potential well and the driving force such as recombination reaction of free radicals. The flatness of the potential for (1,4) to (1,7) configurations on the singlet PES and triplet PESs may be a strong indication that the force on HO_2 and OH radicals on water surfaces is dominated by the local hydrogen bonding to the water molecules and hinders the radicals from recombining by the local potential barrier. Furthermore, the barrier of configuration (1,4) is the last barrier toward strong interaction of (1,2) and (1,3) configurations.
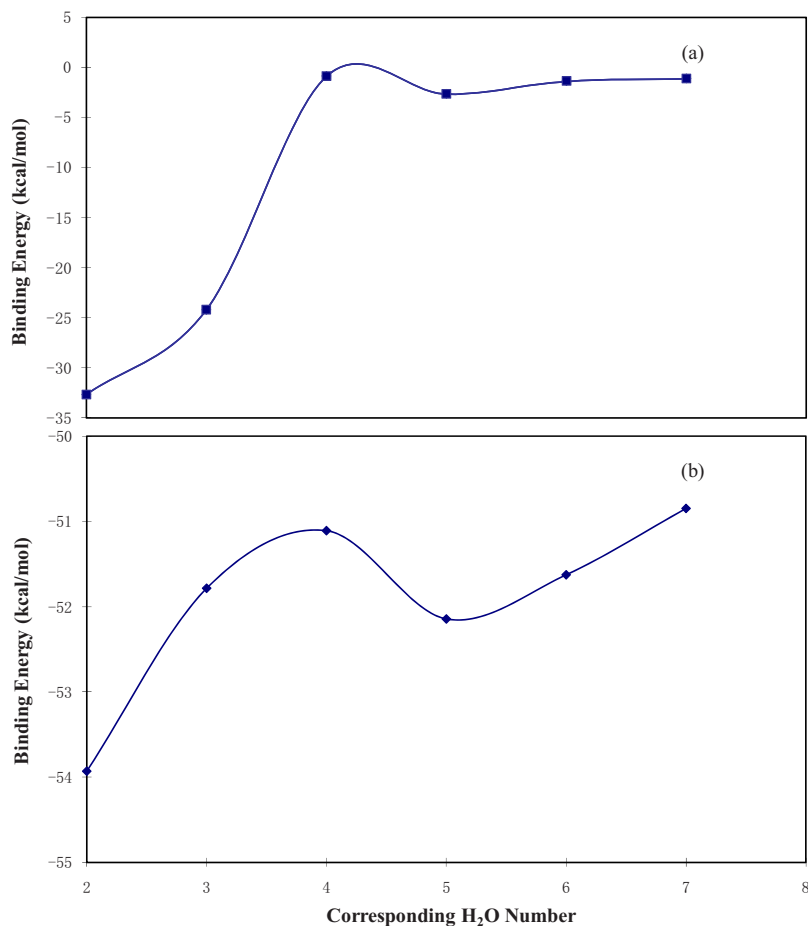
FIG. 5. (Color online) The BE of $(HO_2)_2(H_2O)_7$ for different positions of the radicals as shown in Fig. 4: (a) singlet PES and (b) triplet PES.

In order to understand how the highest occupied molecular orbital of the two radicals mixes and support the discussion on the strength of the bonding effect between the free radicals along the reaction path, the natural bond theory is used to give a picture. Results are shown in Fig. 6 for OH and Fig. 7 for HO_2 with (a) for singlet and (b) for triplet multiplicity, respectively. The singlet occupied lone pair orbitals in the HO_2 and OH radicals are calculated at the level of B3LYP/6-31G(d). For the case of OH radical in the singlet PES, there is no obvious orbital overlapping before the moving OH radical are in position 2. When the two radicals are in (1,2) configuration, the strong overlapping can be seen and a chemical bond between the two O atoms in OH radicals is formed. This is also reflected by the potential drop in the energy curve shown in Fig. 3(a). In the triplet PES, there is no strong influence between the lone pair orbitals from (1,2) to (1,7) configurations, which is also consistent with the moderate energy change for the triplet PES shown in Fig. 3(b). Although the (1,3) configuration is missing, this is the stage that the mixing of the two lone pair orbital is half completed, given that a chemical bond is fully formed in (1,2) configuration and that there is no noticeable orbital in-
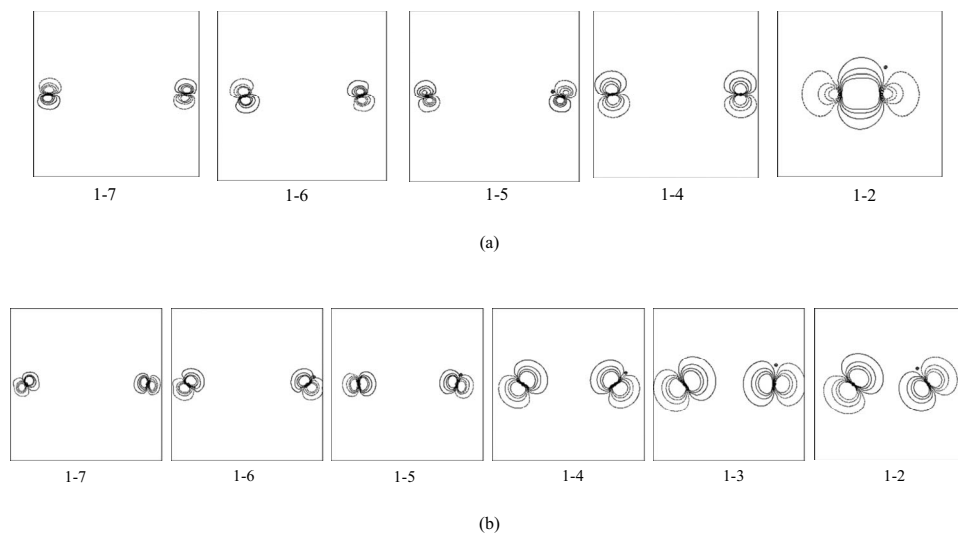

FIG. 6. Contours of the lone pair orbitals interactions of the O atoms in the two OH radicals by NBO analysis: (a) singlet PES and (b) triplet PES.
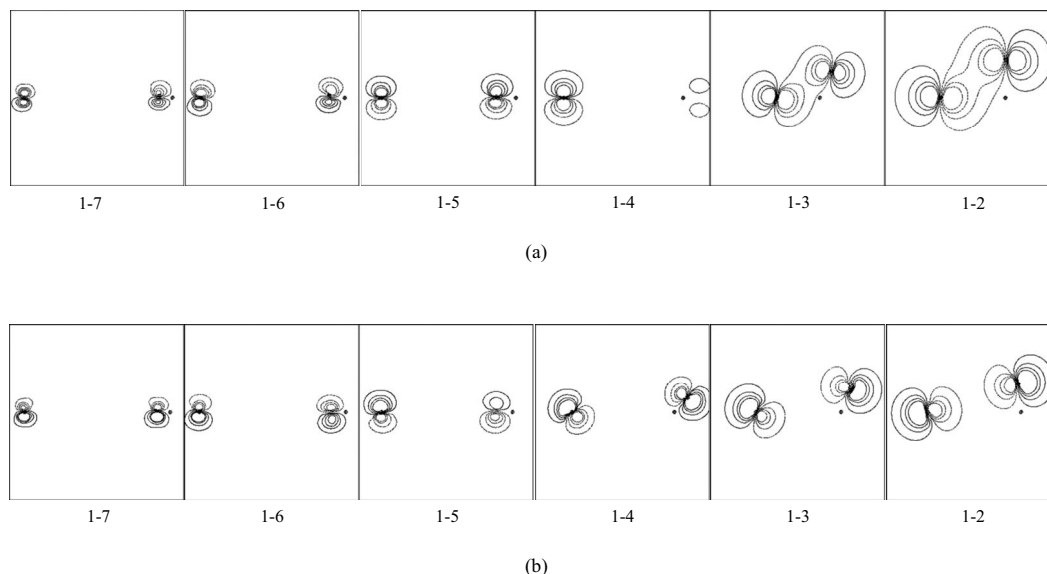
(a)

(b)

FIG. 7. Contours of the lone pair orbitals interactions of the end O atoms in the two HO_2 radicals by NBO analysis: (a) singlet PES and (b) triplet PES.

teraction in the (1,4) configuration. About the HO_2 radical, similar phenomena can be seen. In the singlet PES, the orbital interaction of the two HO_2 radicals is found to be strong for (1,2) and (1,3) configurations and no obvious mixing of lone pair orbitals is found from (1,4) to (1,7) configurations. In the triplet PES, the two half-filled lone pair orbitals do not interact throughout all the configurations. The above data and the pictorial depiction showing the evolution of the wave functions in the process two radicals recombine are consistent with the discussion from the energy curves. This is a strong indication that two lone pair orbitals of OH or HO_2 radical start to have strong interaction in the singlet PES at the distance determined by the two hydrogen bonds formed by three adjacent H_2O molecules, 5.7 Å. This may be thought of as the minimum distance for two free radicals to be stable.

In the triplet PES, Anglada et al.[69] found that the strong negative dependence of production of O_2 on temperature can be attributed to hydrogen bonding between two HO_2 radicals. This means that the hydrogen bonding does have a strong effect on the kinetics of the HO_2. In this work, the linear water cluster provides more hydrogen bonding sites to form local potential wells and thus gives more hindrance for the association of free radicals. Hence, the influence of H_2O molecule for both OH and HO_2 free radicals can be thought of as "repulsive" with respect to their recombination reaction. This may suggest that the interaction of free radicals on the surfaces with available hydrogen bonding sites is an analog of the RCB potential with the short-range attractive force still brought by electron pairing, differing only in that the long-range repulsion is not Coulombic but hindrance introduced by local hydrogen bonds. The free radical interaction on the surface of aerosols includes several processes. The radical firstly diffuses from the air and accommodates onto an aerosol surface and then it can interact with the surface molecules such as H_2O by van der Waals force, in atmospheric conditions, hydrogen bonding. The radical can thus exist on the surface by local stabilization. In the next stage,

by thermal motion, the radical may bond to different surfactant molecules, which is accompanied by breaking and forming hydrogen bonds. Energetically, in this process the radical will pass the local energy barrier and reach different minima in the PES. In the third stage, if the motions of many radicals are in the similar mode, it is possible that two radicals will move to a distance so close that chemical bond formation may occur. When this happens, two radicals will have a tendency to form a stable molecule, so this process is "short range" and "attractive" for the radicals. Simultaneously, the radicals have to break the hydrogen bonds along the reaction path. This means that the barrier for this recombination reaction is mainly provided by local hydrogen bonds and the weak bonds are "repulsive" with respect to the recombination. Since the hydrogen bonds are usually much weaker than a normal chemical bond, the barrier is effective only when two free radicals are far enough so that the local van der Waals interaction can be comparable to the strong electron pair energy, which means that this repulsion is a "long-range" effect. At the final step, the fate of the radical is to form a stable molecule with other open-shell systems by recombination reaction. So the substantial description of the whole process is the competition between the short-range attraction and long-range repulsion. It means that that we can use a scheme similar to the RCB model to predict the recombination of free radicals by using the formula as follows:

$$E_{bar}(r) = nE_{rep}(r) + E_{att}(r) + E_{diff}(r). \qquad (2)$$

In Eq. (2), r is the vector between the two free radicals, n is the number of local interactions, e.g., hydrogen bonds, the free radical has to overcome before recombination reaction, E_{rep} is defined by the negative local interaction energy, E_{att} is recombination energy to form new species, and E_{diff} is the diffusion energy needed to bring the two radicals to the surface. The sum of the above energies gives E_{bar}, the energy of repulsive van der Waals barrier analogous with RCB, of the recombination of two free radicals. $E_{rep}(r)$ is the BE of the free radical on the surface and can be calculated as follows:
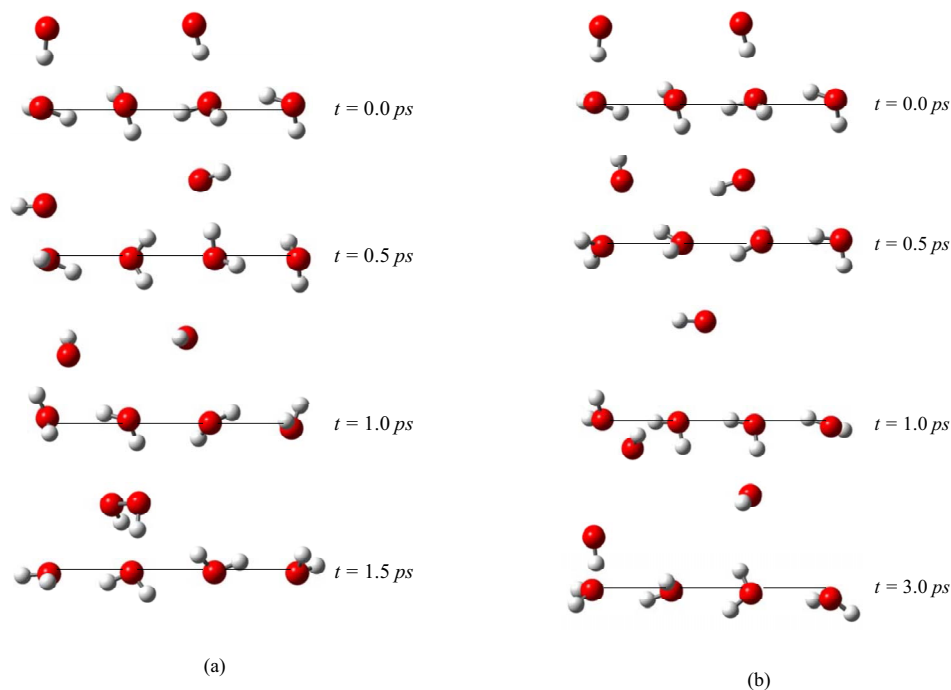
FIG. 8. (Color online) *Ab initio* molecular dynamics with Car–Parrinello scheme simulations for the interaction of the two radicals OH in the presence of water clusters. The starting position at $t=0$ is (1,3): (a) the reaction on the singlet PES is very fast and occur on time scale of about 1.5 ps and (b) no reaction occurs on the triplet PES.

$$E_{rep}(r) = E_{H\,bond} = E_{radical+surface} - E_{radical} - E_{surface}. \qquad (3)$$

$E_{att}(r)$ is the orbital overlapping between the two free radicals, which can be estimated by calculating the BE of the free radical at the surface geometries.

Our calculations show that the (1,4) configuration has E_{bar} values of 8.0 kcal/mol for OH radical and 12.1 kcal/mol for HO$_2$ radical. The values are obtained by assuming $E_{diff}=0$. These are important because (1,4) configuration is geometrically closest to the one that has strong interactions such as (1,3). The E_{bar} of OH association is much lower than that of HO$_2$ because the molecular geometry of HO$_2$ help forms more stable hydrogen bond with H$_2$O molecules on the surface. It is predictable that this energy will increase if the radicals are farther than the (1,4) configuration with the assumption that the reaction occurs along the surface of the water cluster. This assumption implies that the free radical will have to overcome all the local hydrogen bonds in the path in order to react. However, when the distance between the free radicals is long, they will probably not be kept along the surface but be desorbed back into the gas phase. Then the free radical will be adsorbed onto the surface on a position with a lower barrier, e.g., (1,4) or (1,5). In that case, E_{diff} may be important and should be included.

Although the strong interaction is found at the distance of 5.7 Å, provided by the hydrogen bonds of three adjacent water molecules, it is necessary to directly examine whether the strong interaction will lead to free radical association. For this purpose, the *ab initio* molecular dynamics calculations with Car–Parrinello scheme (CPMD) calculations are performed. In our CPMD calculation, the (OH)$_2$(H$_2$O)$_4$ complexes are used since there is no strong wave function mixing found when two radicals are separated by more than four H$_2$O molecules. The formation of H$_2$O$_2$ by two OH radicals on the singlet PES is confirmed. The time was 1.0 ps and 1.5 ps in the singlet PES for (1,2) and (1,3), respectively. The

trajectory calculated with (1,3) initial configuration is shown in Fig. 8. The results show that when the two radicals are separated by two or three H$_2$O molecules, the hydrogen bonds are not strong enough to have a significant impact on the reactivity of the radicals and cannot keep the radicals in an unreactive state. However, the dynamics with the (1,4) initial configuration, the simulation is performed up to 5.0 ps and no reaction is observed. These give direct evidence that strong orbital mixing causes the recombination of two free radicals and the barrier of (1,4) configuration has a lagging effect on the recombination. This confirms that the repulsive barrier can influence the reaction kinetics of species on water surfaces.

IV. CONCLUSIONS

In this work, we studied the interaction of OH radical and HO$_2$ radicals on a linear water cluster. From our quantum chemical calculations the lone pair orbital of the radicals will not have strong interaction that leads to recombination before the two radicals are bound on the position of (1,3) H$_2$O molecules, which has the effective radius of 5.7 Å. This is confirmed by a CPMD simulation on two OH radicals. From these calculations, we can state that the recombination reaction occurring on the aerosol in the atmosphere is strongly affected by the surface water molecules. At present, it has been demonstrated that the H$_2$O molecules in gas phase may behave as a chaperon molecule to catalyze many atmospherically important reactions.[10,11] However, the liquid water molecules or large water clusters in the gas phase may also form energy barrier on free radical reaction by dissolving radicals or forming local hydrogen bond according to this work. This means that the accommodation of free radicals onto aerosols that can provide a matrix of recombination and simultaneously the barrier of the association should be re-evaluated. Since this barrier can be used to estimate the mini-

mum distance of two stable free radicals, the possibility for the prediction of the accommodation ability of aerosol and water droplet in the atmosphere is provided. It is found that a minimum of three water molecules are needed to bind two free radicals in order to separate them from falling into a barrierless zone on the PES leading to recombination reaction. This provides a new piece of information required to access the maximum number of free radicals an aerosol or water droplet can hold as an unreactive state and is especially important for the situations when the equilibrium constant by itself cannot accurately estimate the uptake rate, such as in the troposphere where the free radical concentration is very high. The estimation of the barrier given in this work may provide a new insight of free radical chemistry in the atmosphere.

The model presented in this study allows us to perform exact *ab initio* calculations to understand the interactions between two free radicals. However, a cluster of seven water molecules does not present an aerosol surface. It is necessary to include more water molecules in order to accurately describe the interactions between free radicals on cloud droplet. One way to improve the calculation is by the simulation for radicals interacting with bulk water. This can be carried out effectively by the quantum mechanics/molecular mechanics method. Research is under way to perform this calculation.

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