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Ab Initio Molecular Dynamics Study of the Electronic Structure of Superoxide Radical Anion in Solution

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Received: October 20, 2008; Revised Manuscript Received: November 20, 2008

Ab intitio molecular dynamics simulation of the electronic structure of the aqueous superoxide anion (O_2^-) has been carried out using the Car–Parrinello density functional theory at 298 and 310 K. The modeling system consists of one O_2^- solvated in 31 water molecules. On the basis of our 40 ps production run, the novel mechanism and the nature of the hydration of the superoxide anion in a relatively big aqueous environment have been revealed by using various radial distribution functions. The averaged coordinated water number was estimated to be 4.5. The calculated microscopic configurations of the first solvation shell are in good agreement with the experimental results. The vibrational frequency of the solvated O_2^- anion was red-shifted significantly in comparison with that of the free radical anion in the gas phase. The diffusion coefficient of O_2^- was estimated to be about 8×10^{-5} cm^2/s at 298 K. Comparisons with the previous force-field-based classical molecular dynamics simulations have been made, and the differences were discussed.

I. Introduction

The superoxide radical anion (O_2^-) has attracted considerable attention because of its great importance in biochemical processes[1,2] and in atmospheric chemistry.[3–5] The microscopic structures and electronic properties of the superoxide radical in aqueous environment are highly desired in order to understand its reactivity in solution (e.g., the conversion of O_2^- to O_2 and H_2O_2 catalyzed by the superoxide dismutase enzymes, SOD).[6]

The hydrated O_2^- gaseous clusters, namely $O_2^-(H_2O)_n$ ($n \leq 6$), have been studied both experimentally and theoretically. The heat of hydration of $O_2^-(H_2O)_n$ ($n \leq 3$) was measured using high pressure mass spectrometry by Arshadi and Kebarle.[7] Photodissociation of the clusters was studied by a few groups using photoelectron and photofragment spectroscopy.[8] The structures of $O_2^-(H_2O)_n$ have been examined by Weber and coworkers using Ar nanomatrix isolation infrared spectroscopy.[9] It was found that the most stable cluster shows a tetracoordinated geometry, consisting of two dimeric water subclusters on each side of O_2^-. Each water molecule forms a hydrogen bond to one lobe of the partially filled π^* orbital of O_2^-. Luong and coworkers suggested the similar structure using photoelectron multiple photo-fragment coincidence spectroscopy.[10]

Theoretically, the gaseous structure of $O_2^-(H_2O)_4$ has been simulated using the Kohn–Sham formulation of density functional theory (DFT) with a plane wave basis set by Kuo and Tobias.[11] It was found that the superoxide tetrahydrate complex is highly symmetric and very stable even at 111 K. The calculated vibrational spectrum was in reasonable agreement with experimental spectra.[9] A variety of the bonding scenarios in the larger cluster $O_2^-(H_2O)_6$ were calculated by Antonchenko and Kryachko at the B3LYP/6-311++G(d,p) level of theory.[12] A few lower-energy water hexamers such as ring, chair, prism, and cage were proposed.

The solvation structure of O_2^- in D_2O has been determined with use of electron spin–echo modulation at 4.2 K.[13] It was demonstrated that, in the first solvation shell, each O_2^- is surrounded by four water molecules. The distance between the center of O_2^- and the nearest deuteron of a water molecule is 2.4 Å, while the distance to the next nearest deuteron on the same water molecule is about 1 Å longer (e.g., 3.4 Å). A classical molecular dynamics (MD) simulation of the O_2^- anion solvated in 216 water molecules has been done by Shen, Wong, and McCammon (SWM).[14] The potential energies were calculated using the parameters of carbonyl oxygen for the oxygen atom of O_2^- and the SPC (also SPC/E) models for water taken from the GROMOS force-field. The calculated Helmholtz free energy of hydration of O_2^- was in agreement with the experimental data.[7] However, the hydration number was calculated to be 7.7, in contrary to the experimental value of 4.[13] The diffusion coefficient of O_2^- in water was predicted to be 1.6×10^{-5} cm^2/s at 298 K.

To further advance our understanding of the interaction between O_2^- and water, we have performed the long time scale ab initio simulation for the superoxide anion solvated in waters using the Car–Parrinello molecular dynamics (CPMD) method based on the Kohn–Sham density functional theory and plane wave basis set. Some novel features of the nature of hydration of superoxide anion in a relatively large aqueous environment have been revealed in this work. After a short description of the computational methods in Section II Computational Methods, the radial distribution function, the coordination characteristic, the orientation of the hydrogen bonding, vibrational spectra, and diffusion properties are detailed in Section III Results and Discussion. Some concluding remarks are presented in Section IV Conclusions.

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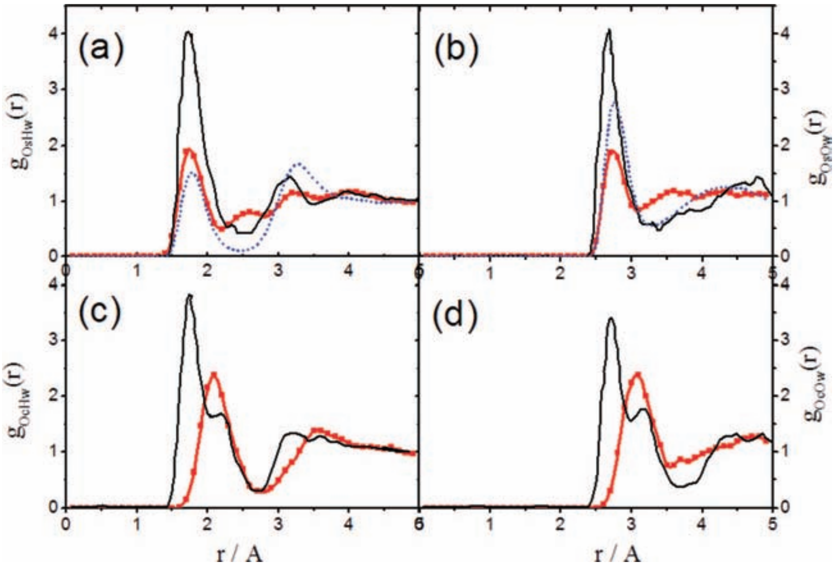

Figure 1. Radial distribution functions (a) g_{OsHw}, (b) g_{OsOw}, (c) g_{OcHw}, and (d) g_{OcOw}. The current ab initio MD calculated data are shown by red lines with symbols. The force-field simulations obtained by SWM (ref 14) are shown in black lines. The dotted lines in (a) and (b) represent the g_{OwHw} and g_{OwOw} functions for pure D_2O. The temperature is 298 K.

II. Computational Methods

All MD simulations were carried out using the CPMD program,[15] which is an implementation of the original Car−Parrinello ab initio molecular dynamics scheme.[16] The local spin density approximation (LSDA) functional theory and the Becke, Lee, Yang, and Parr (BLYP) exchange-correlation functional were employed in the calculation.[17] The nonlocal norm-conserving Troullier−Martins pseudopotentials transformed to a fully nonlocal form using the scheme of Kleinman and Bylander were used to describe the valence-core interactions.[18] The valence electronic wave functions were expanded in a Γ-point plane-wave basis set with an energy cutoff of 70 Ry. The equations of motion were integrated using the Verlet scheme with a time step of 5 au (0.121 fs). Hydrogen nuclei were treated as classical particles with the mass of the deuterium isotope. The fictitious electronic mass was set to be 800 au. The fictitious electron kinetic energy and the dynamics of atoms were controlled by a chain of three Nose−Hoover thermostats.[19] Two simulations were carried out at 298 and 310 K, respectively. The canonical ensemble (NVT) and the periodic boundary conditions were considered in the work.

For reference, the pure water system consisting of 32 D_2O molecules was calculated as well. The length of cubic cell is 9.85 Å with a density of 1.0 g/cm^3. The model system for the aqueous O_2^- solution was prepared by mutating one water molecule to O_2^-. The periodic cell was expanded slightly to 9.93 Å. It corresponds to a concentration of 1.7 M for superoxide anion.

For each system, 10 ps of NVT molecular dynamics simulations were used for equilibration, and subsequently, another 40 ps simulations were carried out for production and were averaged for analysis. The atomic coordinates and velocities along the trajectories were collected every 10 time steps (1.21 fs). During the simulations, the temperature was well controlled, and the averaged fictitious kinetic energy was maintained stably at a level of 0.030 hartree. The total energy was conserved with a deviation of only 0.00065 hartree. A similar theoretical scheme has been used successfully in the simulations of the $O_2^-(H_2O)_4$ cluster and numerous aqueous systems.[20]

III. Results and Discussion

For convenience, the two oxygen atoms and the center of mass of the superoxide anion were denoted as Os and Oc, respectively. The oxygen and hydrogen atoms of water molecules were marked with Ow and Hw, respectively. The results deduced from the 40 ps production run were presented.

1. Radial Distribution Function (*g*(*r*)). The $g_{OsHw}(r)$ function is shown in Figure 1a. The data obtained from molecular mechanics by SWM is also included for comparison. According to SWM's results,[14] the first peak is at 1.7 Å with a height of 4.0, corresponding to the distances for the hydrogen bonding between Os and Hw atoms in the first solvation shell. The first minimum was found at 2.3 Å. There is a minor shoulder after the minimum followed by the second peak at 3.2 Å. However, our ab initio calculations reveal a different mechanism. As can be seen in Figure 1a, the calculated $g_{OsHw}(r)$ curve is rather diffuse (i.e., less sharply peaked than SWM's results). The first peak is located at 1.74 Å, slightly longer than SWM's result. Moreover, the height of the peak is only 1.9, which is only half of the corresponding SWM's result. The first minimum is at 2.20 Å. There is a shoulder spanned between 2.20 and 2.80 Å, which is more significant than that in SWM's result. Through the analysis of the trajectories, it was found that this shoulder corresponds to the distances between the Hw atom forming hydrogen bond with one Os and the other Os. It implies that each Hw atom could form two hydrogen bonds with the two Os atoms simultaneously. One is relatively stronger, as indicated by the shorter OsHw distance (e.g., the first peak of g_{OsHw}), and the other is weaker, as indicated by the shoulder of g_{OsHw}.

The $g_{OwHw}(r)$ function for pure water has been shown in Figure 1a as well for comparison. Evidently, the first peak of $g_{OsHw}(r)$ is at a shorter distance (by 0.04 Å) with the higher population (by 0.4) than that of $g_{OwHw}(r)$. It shows that O_2^- is a stronger proton acceptor than the water molecule, in accordance with the fact that the proton affinity of O_2^- (15.3 eV) is about twice of that of water (7.1 eV). Moreover, as shown in Figure 1a, the closest distance between Os and Hw is around 1.30 Å, which is slightly shorter than that for OwHw in $g_{OwHw}(r)$ (ca. 1.40 Å). This phenomenon shows that superoxide anion might form strong proton-shared or an ionic hydrogen bond with water molecules. However, since the proton transfer reaction $O_2^- + H_2O \rightarrow HO_2 + OH^-$ is highly endothermic by up to 53 kcal/mol, superoxide anion is still a weaker base than hydroxide anion. Concerning the structure of the first solvation shell, the first minimum and the second peak of $g_{OsHw}(r)$ are both less pronounced than those of $g_{OwHw}(r)$ and shift to shorter distances, it implies that the first solvation shell of O_2^- is comparatively less structured than that in pure water.

To further reveal the hydrogen-bonding mechanism in the first solvation shell, the $g_{OsOw}(r)$ curve is shown in Figure 1b. The first peak is at 2.70 Å. Although the peak in SWM's calculation is at the similar position, it is significantly higher than that in this work. Moreover, the present ab initio simulation shows a broad shoulder after the first peak, which corresponds to the doubly hydrogen-bonding feature mentioned above. This shoulder is almost invisible in the force-field MD calculation of SWM. In comparison with the $g_{OwOw}(r)$ function of pure water, the first peak of $g_{OsOw}(r)$ drops by about one-third. Moreover, the first minimum shifts from 3.25 Å to 3.06 Å, and the curve is almost flat after it. This feature confirms that the first solvation shell of superoxide anion in solution is less structured, which is in accordance with the conclusions drawn from the $O_2^-(H_2O)_6$ cluster.[12] On the other hand, it is worth noting that the $g_{OwHw}(r)$ and $g_{OwOw}(r)$ functions for the superoxide solution are nearly the same as those for pure water. The presence of 1.7 M O_2^- has no pronounced distortion to the hydrogen-bond network of the bulk water.

The $g_{OcHw}(r)$ and $g_{OcOw}(r)$ functions are shown in Figure 1c and d, respectively. As can be seen from the $g_{OcHw}(r)$ curve, the first peak, corresponding to the distance between the center of superoxide and the nearest deuteron of a water molecule, is centered at 2.1 Å. The second peak, corresponding to the distance to the next nearest deuteron of the same water, is centered at 3.5 Å. Both values are in reasonable agreement with the respective experimental data of 2.4 and 3.4 Å.[13] The 0.3 Å difference in the first distance may be caused by the very low concentration of O_2^- (0.1 mM) used in the solid matrices experiment in comparison with ours 1.7 M.

In regards to the force-field MD data obtained by SWM, the present ab initio MD gives completely different $g_{OcHw}(r)$ and $g_{OcOw}(r)$ functions. First, the peaks in ab initio MD systematically move to longer distances by about 0.4 Å; second, the first peaks in force-field MD are much higher; third, the visible shoulders after the first peaks in force-field MD disappear in ab initio MD. Such differences may indicate the importance of the electronic interaction in the present negatively charged radical anion-solvent system. The empirical parameters of the force-field used in the O_2^--water simulation have to be improved.

The radical distribution functions were calculated at 310 K as well to understand the in vivo structure of the O_2^- solution. Basically, the curves are very similar to those obtained at 298 K in view of the positions and shapes of the peaks. The only noticeable change is that the heights of the peaks are lowered slightly as the temperatures increase especially for the first peak, implying that the hydrogen bonding is weakened somewhat due to the thermal effect.

2. Coordination Numbers (N_w). The coordinated water numbers N_w in the first solvation shell of the superoxide anion were calculated by integrating the envelop of the radial distribution function from the onset of the first peak to the first minimum. The results obtained from $g_{OsHw}(r)$, $g_{OsOw}(r)$, $g_{OcHw}(r)$, and $g_{OcOw}(r)$ are 4.5, 4.8, 4.6, and 4.9, respectively. The average value is 4.7, which is in agreement with the experimental measurement that each superoxide is surrounded by about four water molecules. In contrast, the force-field MD study of SWM obtained a value of 7.7, which deviates from the present ab initio MD result significantly.

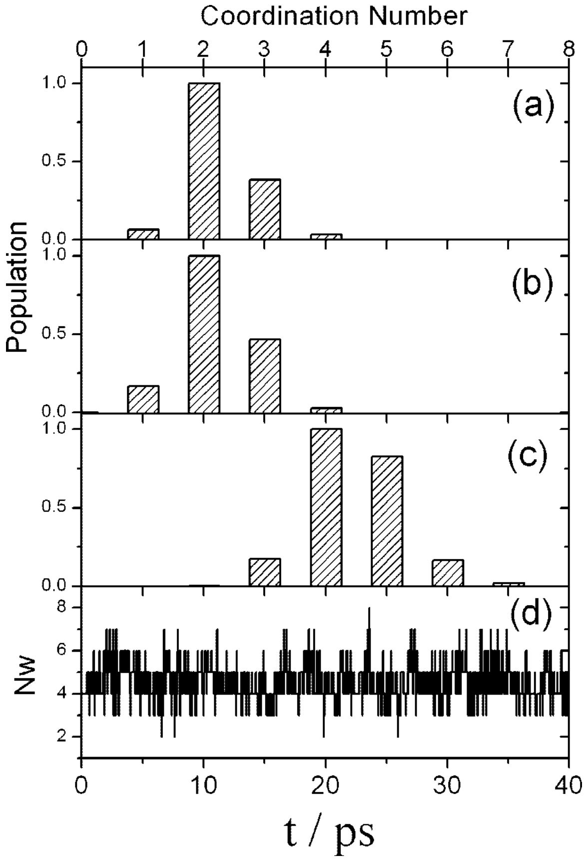

Figure 2. Histograms of the coordination water numbers for (a) Os atom, (b) the other Os atom, (c) the sum of two Os atoms in the first solvation shell, and (d) the temporal profile for the total coordination water number in a duration of 40 ps. The temperature is 298 K.

To gain an insight into the dynamic structure of the first solvation shell, the running coordination numbers for each oxygen atom of superoxide anion have been calculated. Hydrogen bonding was assumed to occur when the distance between Hw and Os is less than 2.2 Å (e.g., the first minimum of the $g_{OsHw}(r)$ function). The results are shown in Figure 2a–d. As can be seen from Figure 2a and b, the calculated coordinated numbers are nearly equivalent for the two Os atoms with the prevalent number of 2. This is an indication that the net charge is delocalized over the OO bond. The total coordination histogram (Figure 2c) shows that the most significant numbers are 4 and 5 (in average, 4.5), which is in good agreement with the integration coordination number as mentioned above. A temporal change of the total coordination number is shown in Figure 2d. Apparently, the large fluctuation occurs. The prevalent values fluctuate between 4 and 5, with a minor contribution from 3 and 6. A few configurations do involve high coordination number up to 7 and even 8 or low coordination number down to 2.

As the temperature increases to 310 K, the average coordination number was calculated to be 4.3, which is slightly smaller than that at 298 K.

3. Orientation of the Hydrogen Bonds. The orientations of water molecules toward superoxide anion in the first solvation shell are characterized using four angles, including two bond angles (α, β) and two dihedral angles(ϕ_1, ϕ_2), as shown in the insert configuration in Figure 3. The α angle is distributed

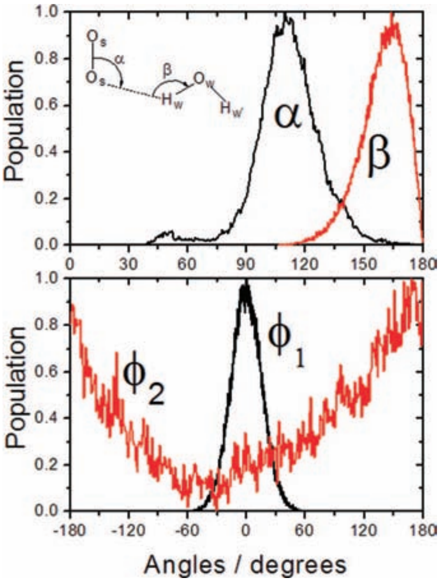

Figure 3. Orientations of the water molecules in the first solvation shell toward superoxide anion. Angles are shown by the model in the insert. Upper panel: α, β; Lower panel: ϕ_1(OsOsHwOw), ϕ_2(OsHwOwHw′).

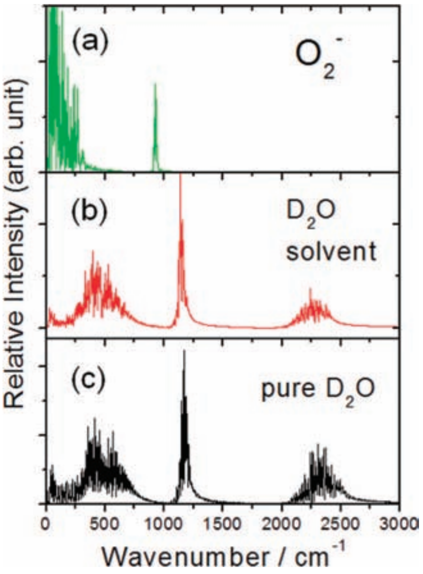

Figure 4. The vibrational power spectra for (a) O_2^-, (b) bulk waters in the O_2^- solution, and (c) pure waters. The spectra are obtained by the Fourier transformations of the velocity autocorrelation functions.

widely from 30 to 180° with a main peak centered at about 104−110°. This feature supports the bonding model for the hydrogen-bonding interaction in the O_2^- solution, as suggested by spin−echo and infrared spectroscopy experiments.[9,13] A minor peak centered at about 50° indicates the circumstance that one Hw atom is bonding to two Os atoms simultaneously, as mentioned above. The other angle β shows an unsymmetrical curve, spreading in the range 120−180° and centered at 158−168°. This is a typical geometry for a hydrogen bond with a nearly linear intermolecular bond angle.

The relative orientation between the Os−Os bond of O_2^- and the Hw−Ow bond of water is denoted as ϕ_1. As can be seen in Figure 3, the ϕ_1 angles have only one sharp peak centered at 0°. This feature supports the spin−echo experiment that the O_2^- and nearest O−D bonds were found to be coplanar.[13] ϕ_2 represents the dihedral angle of Os−Hw−Ow−Hw′, showing the direction of the other O−D bond toward the planar hydrogen bonds. Apparently, this O−D bond may rotate from −180 to 180°. However, it prefers to form a nearly trans configuration laying at the same plane of the hydrogen bond. Alternately, the O−D bond may be perpendicular to the hydrogen-bond plane, as suspected from the spin−echo experiment,[13] because the populations of ϕ_2 around 90° are nearly 50%. The minor peaks around 0° correspond to the geometry of the gaseous $O_2^-(H_2O)_4$ cluster.[9,11]

4. Vibrational Spectra. The vibrational densities of states (VDOS) of various atoms have been calculated using the Fourier transformation of the velocity autocorrelation function (VACF). The power spectrum of O_2^- in solution, which includes both infrared and Raman features, is shown in Figure 4a. The peak centered at about 920 cm^{-1} corresponds to the normal vibrational mode of O_2^- anion. For the free O_2^- radical in the gas phase, the harmonic frequency was calculated to be 950 cm^{-1} using the CPMD program. Therefore, the frequency of O_2^- in solution might be red-shifted. The massive peaks between 0 and 300 cm^{-1} are due to both the intermolecular modes and the numerical noise.

The VDOS spectrum for pure water (D_2O) is also shown in Figure 4c for reference. Three major vibrational modes centered at 500, 1170, and 2250 cm^{-1}, respectively, are in good agreement with the experimental and theoretical results.[21] The VDOS spectrum for the water as the solvent in the O_2^- solution is shown in Figure 4b for comparison. With the presence of superoxide anion at low concentration (1.7 M in this work), the spectra of water are only slightly disturbed. The stretching and bending modes are slightly red-shifted whereas the other modes together with those for the intermolecular vibrations have little change. Meanwhile, the vibrational spectra do not change significantly as the temperature increases to 310 K.

5. Diffusion Coefficients. The diffusion coefficient of O_2^- in water was calculated using both the mean-squared displacement (MSD) and the VACF methods. At 298 K, the diffusion coefficient was obtained to be 9.7 and 7.1 ($\times 10^{-5}$ cm^2/s) using MSD and VACF, respectively. Obviously the two data are in good agreement. In comparison with the force-field calculated result of 1.6×10^{-5} cm^2/s at 298 K by SWM,[14] our diffusion coefficient is significantly higher. This difference is reasonable because, in SWM's calculation, two times more water molecules are coordinated to the O_2^- radical and thus the diffusion of O_2^- radical might be slow down. Moreover, only 10 ps MSD was used in SWM's work.

As expected, at higher temperature of 310 K, the diffusion coefficient of O_2^- in water tends to be larger. The calculated data from MSD and VACF are 9.7 and 8.7 ($\times 10^{-5}$ cm^2/s), respectively. It is worth noting that the reported diffusion coefficients are only meaningful qualitatively because of the small cubic cell without the consideration of the counterions and the finite simulation time.

IV. Conclusions

The microscopic structure of the first solvation shell of superoxide anion in water has been revealed in detail using the periodic cubic cell with 32 molecules (1 O_2^- + 31 D_2O) and the ab initio CPMD simulations. It is shown that superoxide anion acts as a strong proton acceptor, interacting with at least four water molecules through hydrogen bonding. Stronger proton-shared or an ionic hydrogen bond between O_2^- radical and water molecules might exist as well. The first solvation shell is less structured than those in pure water. The distance between the center of superoxide and the nearest hydrogen atom of water is about 2.1 Å, and the distance for the other hydrogen of the same water is 3.5 Å. The coordinated number was estimated to be 4.5. The theoretical results are in reasonable agreement with the experimental measurements. In view of the vibrational spectra, it was found that the frequency of O_2^- radical is red-shifted by about 30 cm^{-1} in solution with respect to the gaseous molecule. The diffusion coefficient of O_2^- in water was calculated to be about 8×10^{-5} cm^2/s at 298 K. Temperature dependence of the solvation structure, hydrogen bonds, coordination, and vibrational and diffusion properties is weak.

Comparisons with previous force-field based classical MD simulation of the aqueous superoxide anion have also been made. It is shown that the electron correlation plays an important role in the simulation of the structure of the superoxide solution. Improved force field has to be developed for further MD study of the O_2^- solution.

Acknowledgment. This work was supported by NSFC-20673079 and NSFC-20603025 and by FANEDD-200224.

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JP809270D