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Classical molecular-dynamics simulation of the hydroxyl radical in water

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We have studied the hydration and diffusion of the hydroxyl radical OH^0 in water using classical molecular dynamics. We report the atomic radial distribution functions, hydrogen-bond distributions, angular distribution functions, and lifetimes of the hydration structures. The most frequent hydration structure in the OH^0 has one water molecule bound to the OH^0 oxygen (57% of the time), and one water molecule bound to the OH^0 hydrogen (88% of the time). In the hydrogen bonds between the OH^0 and the water that surrounds it the OH^0 acts mainly as proton donor. These hydrogen bonds take place in a low percentage, indicating little adaptability of the molecule to the structure of the solvent. All hydration structures of the OH^0 have shorter lifetimes than those corresponding to the hydration structures of the water molecule. The value of the diffusion coefficient of the OH^0 obtained from the simulation was $7.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, which is higher than those of the water and the OH^- . © 2005 American Institute of Physics. [DOI: 10.1063/1.2013253]

I. INTRODUCTION

The hydroxyl radical OH^0 is a molecule that participates in many events of biophysical importance which includes the removal of heavy metals of contaminated water^{1,2} and the subtraction of protons from the C–C bonds.³ It is formed in different processes such as the radiolysis of water⁴ and the photolysis of dissolved NO_3^- . Knowledge of the hydration of the OH^0 will allow a better understanding of its interaction with different molecules in solution.

Different models of OH^0 have been used to study different processes.^{5–16} Hamza *et al.*⁵ studied the proton subtraction of the C4^* of a DNA sugar using an *ab initio* method. In this case, the charge of the OH^0 is $0.44e$ for the proton, and $-0.44e$ for the oxygen. Cooper *et al.*⁶ carried out an *ab initio* computation of the optimized structures for the $\text{H}_2\text{O}\cdot\text{OH}^0$ complex. They obtained three structures, in two of them the OH^0 acts as proton donor, and in a third it acts as proton acceptor. Hamad *et al.*⁷ studied the hydration of OH^0 in small $\text{H}_{2n+1}-\text{O}_n$ ($n=1-5$) clusters using different quantum-chemical methods. The binding energy is the largest when OH^0 acts as proton donor. Cabral do Couto *et al.*,⁸ with microsolvation modeling and Monte Carlo simulations, analyzed the structure, vibrational spectrum, and energetic of $\text{OH}^0\text{--H}_2\text{O}$ clusters. Comparing the structures of the hydrated OH^0 solution with the structure of pure liquid water, they found that the OH^0 radical plays a strong role of proton donor in water, too.

Roeselová *et al.*⁹ reported the first classical molecular-

dynamics (MD) study about the behavior of the OH^0 radical in aqueous salt aerosol surfaces, using $0.4e$ for the hydrogen charge, and $-0.4e$ for the oxygen charge. In a recent classical MD study,¹⁰ these authors found that the OH^0 perturbs significantly the structure of water molecules in their first and second solvation shells, indicating that this could be the cause of the surfactantlike behavior of this molecule.

Vácha *et al.*¹¹ calculated the potentials of mean force connected with moving an atmospherically relevant molecule or radical through an aqueous slab by means of MD simulations. They obtained that the OH^0 has a hydrophilic behavior, so that it has lower free energy in water than in air.

Vassilev *et al.*¹² used the Car-Parrinello density-functional theory to perform a MD simulation of a OH^0 and 31 water molecules, obtaining a local structure configuration around OH^0 , with two water molecules bonded to the OH^0 oxygen, one water molecule bonded to the OH^0 hydrogen, and a third water molecule hemibonded to this molecule. Vande Vondele and Sprik¹³ attributed the hemibonded water finding to an artifact of the method. The latter authors performed a density-functional-theory-based MD simulation of the OH^0 radical in solution, where this molecule acts as a good hydrogen bond donor.

Khalack and Lyubartsev¹⁴ compared the behavior of OH^0 and OH^- in liquid water using a Car-Parrinello MD simulation, finding that OH^0 is a more active hydrogen-bond donor and acceptor than the water molecule. Furthermore, they found that the accepted hydrogen bonds for the OH^0 are much weaker than for the OH^- .

In spite of the number of works dealing with the study of the OH^0 radicals, a complete analysis of the hydration and diffusion of OH^0 has not been carried out. The small number of solvent molecules and the small number of configurations

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used in the *ab initio* calculation does not allow a complete and extensive description of the behavior of the OH^0 in solution. By using classical MD it is possible to observe the simulated system visiting most of the possible configurations and obtain several functions and properties that depend on it (e.g., radial distribution functions).

Here we report a study of OH^0 hydration and diffusion using classical MD. We have obtained the most frequent hydration structures of the OH^0 , the lifetimes of these structures, their diffusion coefficients, hydrogen-bond distributions, and the radial (RDF) and angular (ADF) distribution functions. The analysis of the group or results allowed us to obtain a complete description of the behavior of the OH^0 in solution.

We have reported a study of OH^- in extended simple point charge (SPC/E) water model using classical MD in a previous paper,¹⁷ here we compare the results of OH^- and OH^0 simulations and find important differences.

II. METHODS

A. Molecular-dynamics simulation

We carried out MD of OH^0 in solution using the GRO-MOS 96 (Ref. 18) package, in which the equations of motion are integrated by using a leap-frog algorithm.

For the interaction of the atoms i and j of the OH^0 and water molecules, we used the potential

$$U_{ij} = \left[\frac{C_{12}}{r_{00}(i,j)} \right]^{12} - \left[\frac{C_6}{r_{00}(i,j)} \right]^6 + \sum_{\alpha=1}^3 \sum_{\beta=1}^3 \frac{q_{\alpha}(i)q_{\beta}(j)}{r_{\alpha\beta}(ij)}, \quad (1)$$

where the van der Waals interaction involves only oxygen atoms and q the partial atomic charges.

The programs use a twin range method which evaluates the potential energy at every step for short distances ($r < R_p$) and less frequently at longer distances ($r > R_l$). A reaction field is used to approach the contributions of the electrostatic component of the interaction energy for $r > R_f$. We used the van der Waals parameters of MTA1 basis of the GROMOS 96 package, $C_{12} = 2.634 \times 10^{-6}$ kJ mol⁻¹ nm¹² and $C_6 = 2.617 \times 10^{-3}$ kJ mol⁻¹ nm⁶, the cut-off radii $R_p = 1.1$ nm and $R_l = 1.4$ nm for the van der Waals interactions, and the cut-off radius $R_f = 1.4$ nm for the reaction field.

We used the SPC/E model¹⁹ as solvent in which the O-H distance is 0.1 nm, the H-O-H angle is 109.47°, the oxygen atom charge is $-0.8476e$, and the hydrogen atom charge is $0.4238e$. We calculated the charges of the OH^0 atoms using the AIM methods and the HF/6-31G* basis, with the GAUSSIAN 98 package. The atom charges in the OH^0 model are $-0.438e$ for the oxygen and $0.438e$ for the hydrogen. We used the SHAKE method to impose distance constraints on the bond length in the water and in the OH^0 .

We used a previously stabilized configuration of 216 SPC/E water molecules, in which we eliminated four hydrogen atoms to obtain four OH^0 radical molecules to initialize the system. We carried out 50 steps of energy minimization keeping the OH^0 molecules positionally restrained. Then, we stabilized the system by 200 steps of energy minimization without constraints, obtaining a unit cubic cell of 1.87 nm³.

TABLE I. Position of the first and second peaks in the $g(r)$ functions.

$g(r)$	First peak (Å)	Second peak (Å)
$g_{\text{O}^0\text{O}}(r)$	2.85	6.90
$g_{\text{O}^0\text{H}}(r)$	1.97	3.35
$g_{\text{H}^0\text{H}}(r)$	2.40	4.30
$g_{\text{H}^0\text{O}}(r)$	1.75	3.75

Initially, we assigned the velocities of the molecules according to Boltzman's distribution at 100 K. We used the Berendsen's thermostat²⁰ to apply a thermal and a hydrostatic bath to the system, obtaining an isobaric-isothermal ensemble. We raised the temperature to 300 K and the pressure to 1.013×10^5 Pa, over 15 ps. Then, we calculated the trajectory for an additional 2 ns.

In the calculation of the diffusion coefficient we used the expression

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \frac{1}{n} \left\langle \sum_{i=1}^n [r_i(0) - r_i(t)]^2 \right\rangle, \quad (2)$$

where n is the number of molecules and $r_i(t)$ is the position of a molecule atom at time t . This formula is used only for large times, when the diffusive regime is reached.

We considered the residence time (t_r) like the time during which a hydration structure is observed.¹⁷ A histogram of the number of times that a hydration structure is repeated (N_S) as a function of the residence time can be fitted with a single exponential, a characteristic of a Poissonian process, as

$$N_S(t_r) = N_S(0) \exp(-t_r/\tau), \quad (3)$$

where τ is the lifetime, the residence time in which $N_S(t)$ decays at $1/e$ of its value in $t_r=0$.

We used $r_{\text{Hbond}} < 2$ Å as the maximum distance between the oxygen atom and the hydrogen atom that participate in the hydrogen bond, and $\text{angle}_{\text{Hbond}} > 145^\circ$ as the minimum angle formed by the atoms $\text{O}_{\text{donor}}-\text{H}-\text{O}_{\text{acceptor}}$ as requirements for the formation of hydrogen bonds.²¹ In each case, a histogram of the quantity of hydrogen bonds in each atom (or molecule) analyzed is calculated, which is then normalized with the number of trajectories and the number of atoms of the same type (or molecules) in the system.

III. RESULTS AND DISCUSSION

A. Radial distribution functions

We calculated the RDFs [$g(r)$] of solvent atoms around the present atoms in the system. The positions of the peaks of $g(r)$ for the different atoms are shown in Table I.

Figure 1(a) shows the RDF of oxygen water atoms around oxygen atoms of the SPC/E water [$g_{\text{OO}}(r)$], of the OH^- ion [$g_{\text{O}^*\text{O}}(r)$], and of the OH^0 radical [$g_{\text{O}^0\text{O}}(r)$]. If the $g_{\text{O}^0\text{O}}(r)$ is compared with the other two $g_{\text{OO}}(r)$ functions, the height of the maximum (1.4 high) at $r=2.85$ Å is small, and a minimum around 3.3 Å and a second maximum around 4.7 Å are absent in this function. Also, the $g_{\text{O}^0\text{O}}(r)$ maximum is farther from the origin than those of $g_{\text{OO}}(r)$ and $g_{\text{O}^*\text{O}}(r)$. The small $g_{\text{O}^0\text{O}}(r)$ maximum height indicates a poor presence

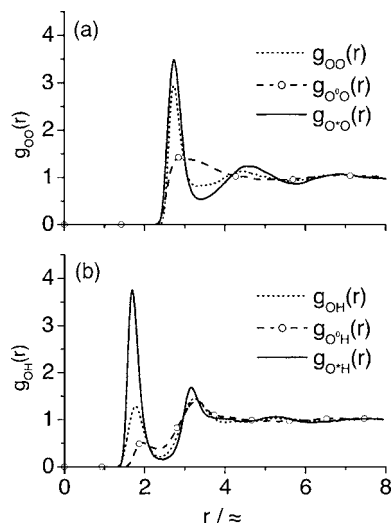


FIG. 1. Oxygen-oxygen (a) and oxygen-hydrogen (b) radial distribution functions. The dotted lines correspond to the RDF of water atoms around oxygen water atoms, the dash-circle lines to the RDF of water atoms around oxygen OH^0 atoms (O^0), and the solid lines to the RDF of water atoms around oxygen OH^- atoms (O^*).

of water oxygen atoms near the O^0 (in the first hydration sphere). The absence of a minimum in 3.3 \AA and a second peak in 4.7 \AA indicate the absence of a solvent structuring in the second hydration sphere of the O^0 .

The first peak of the RDF of water hydrogen around the radical oxygen $g_{\text{O}^0\text{H}}(r)$ at 1.97 \AA is 0.6 high, and the second peak at 3.35 \AA is 1.6 high [Fig. 1(b)]. There is no third small peak at $r=5.2 \text{ \AA}$ unlike in $g_{\text{O}^*\text{H}}(r)$ and $g_{\text{OH}}(r)$. The $g_{\text{O}^0\text{H}}(r)$ local minimum at $r \approx 2.4 \text{ \AA}$ is higher than those of $g_{\text{O}^*\text{H}}(r)$ and $g_{\text{OH}}(r)$. The height of the first $g_{\text{O}^0\text{H}}(r)$ peak indicates a poor presence of hydrogen in $r < 2.5 \text{ \AA}$. Thus, the comparison of the analyses of RDFs $g_{\text{OH}}(r)$ and $g_{\text{OO}}(r)$ allow us to conclude that the solvent structuring around the radical oxygen (O^0) is smaller than the solvent structuring that occurs around the oxygen atoms of the SPC/E water and of the OH^- .

The hydration structure around the radical hydrogen atom H^0 is different from that of the O^0 . The curve of $g_{\text{H}^0\text{O}}(r)$ [Fig. 2(a)] has a first peak at 1.7 \AA , 2.5 high, and it is higher than those of $g_{\text{H}^*\text{O}}(r)$ and $g_{\text{HO}}(r)$. The local minimum at 2.3 \AA is deeper than those of the other two RDFs. The second peak at 3.7 \AA , 1.5 high, is farther from the origin than those of the $g_{\text{HO}}(r)$ and $g_{\text{H}^-\text{O}}(r)$. There is practically no third peak in $g_{\text{H}^0\text{O}}(r)$. The height of the first $g_{\text{H}^0\text{O}}(r)$ peak indicates the almost permanent presence of solvent oxygen atoms in the first hydration sphere of the H^0 . Because of it, the second hydration sphere [associated with the $g_{\text{H}^0\text{O}}(r)$ second peak] is formed at a distance farther from the origin than those corresponding to the water and the OH^- . This analysis permits us to deduce a strong structuring of the solvent around the H^0 . This major presence of water in the first hydration sphere of the H^0 produces the difference in height of the first $g_{\text{H}^0\text{H}}(r)$ peak compared with those of the water and the OH^- [Fig. 2(b)].

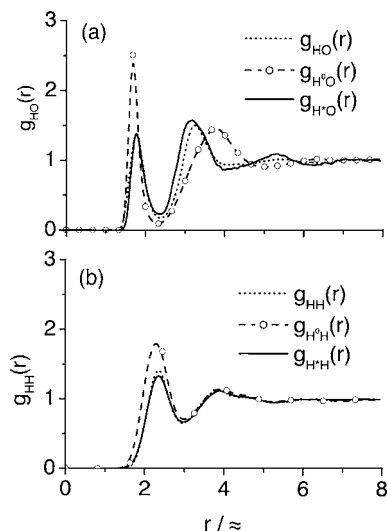


FIG. 2. Hydrogen-oxygen (a) and hydrogen-hydrogen (b) radial distribution functions. The dotted lines correspond to the RDF of water atoms around hydrogen water atoms, the dash-circle lines to the RDF of water atoms around hydrogen OH^0 atoms (H^0), and the solid lines to the RDF of water atoms around hydrogen OH^- atoms (H^*).

B. Angular distribution functions

We found it useful to study the hydration structures in the radical oxygen (O^0) and radical hydrogen (H^0) separately. In the case of the O^0 , we performed the calculation of the ADF, i.e., the plot $P_{\text{H}^0\text{O}^0\text{H}}(\cos \phi)$ —the probability of getting $\cos \phi$ against $\cos \phi$, where ϕ is the angle formed by the atoms $\text{H}^0-\text{O}^0-\text{H}$ (radical hydrogen-radical oxygen-water hydrogen), classifying the $P(\cos \phi)$ functions according to the quantity of hydrogen atoms of water present within a sphere with the center in O^0 . We chose the radius of that sphere equal to the position of the first peak in the RDF $g_{\text{O}^0\text{H}}(r)_{\text{sphere}} = 2 \text{ \AA}$. We defined the hydration structure with at least one hydrogen atom of one water molecule in the sphere as $\text{O}_2\text{H}_3(\text{H}^0-\text{O}^0 \cdots \text{H}-\text{O}-\text{H})$, and with at least two hydrogen atoms belonging to two different water molecules in the sphere as O_3H_5 . Figure 3 shows $P(\cos \phi)$ for the hydration structures. We do not find more than two hydrogen atoms of different water molecules inside the first hydration sphere. A comparative analysis of the occurrence percentages

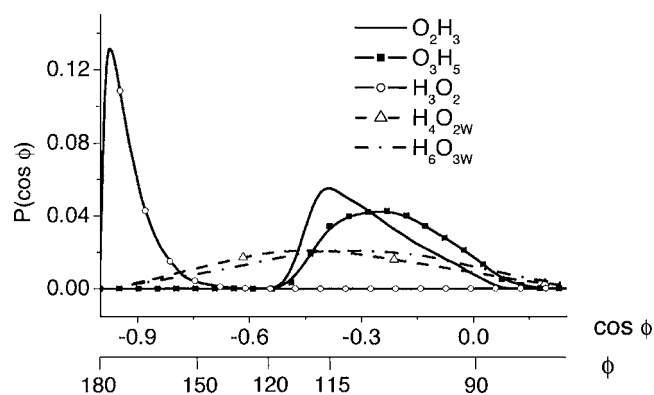


FIG. 3. $P(\cos \phi)$ for the hydration structures in OH^0 and SPC/E water molecules.

TABLE II. Lifetimes, occurrence percentages of the hydration structures (O_p), and peaks of $P(\cos \phi)$ of hydration structures in OH^0 and in SPC/E water molecules.

Structure	Lifetime (fs)	O_p (%)	Peak of $P(\cos \phi)$ ($^\circ$)
H_3O_2	30.2	88.4	165
O_2H_3	35.4	56.7	113
O_3H_5	33.3	27.0	105
O_4H_7	18.2	1.4	...
H_4O_{2w}	43.7	45.7	117
H_6O_{3w}	91.1	53.2	110

of the hydration structures (O_p) and the location of the $P(\cos \phi)$ maxima is shown in Table II. O_2H_3 is the most frequent hydration structure in O^0 .

During 88.4% of the time we found a unique water oxygen atom in the first hydration sphere ($r_{\text{sphere}} = 2 \text{ \AA}$) of radical hydrogen H^0 . We defined this hydration structure on H^0 as H_3O_2 , with a water molecule bound to the H^0 . $P_{\text{H}^0\text{O}^0}(\cos \phi)$ of the hydration structure is also shown in Fig. 5, ϕ being in this case the angle formed by the atoms $\text{O}^0-\text{H}^0-\text{O}$. A structure with two hydration water was detected along the simulation, only $10^{-3}\%$, which can be neglected. Figure 4 shows the hydration structures in O^0 and H^0 .

In the case of water, H_4O_{2w} is the hydration structure

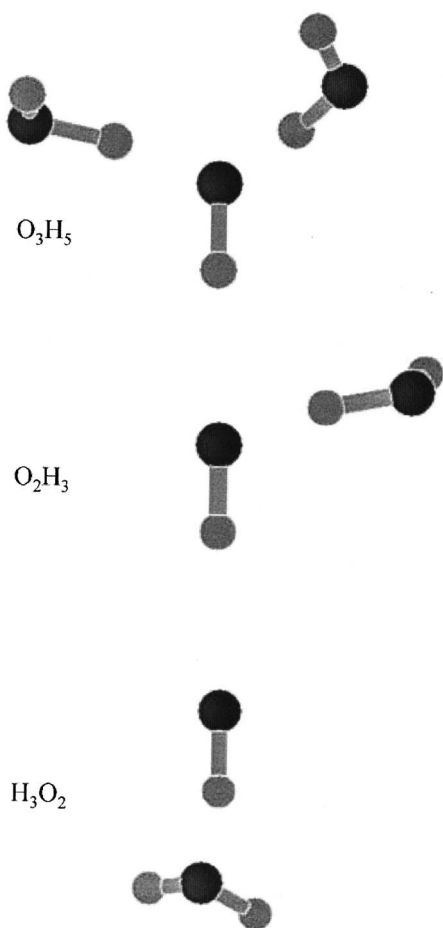


FIG. 4. Hydration structures in the OH^0 oxygen ($\text{O}_3\text{H}_5, \text{O}_2\text{H}_3$) and in the OH^0 hydrogen (H_3O_2). The gray spheres represent hydrogen atoms and the black oxygen atoms. The molecular bonds are indicated by gray cylinders.

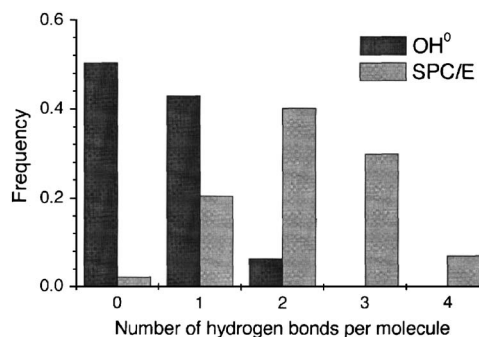


FIG. 5. Hydrogen-bond distributions per molecule for the OH^0 and SPC/E water molecules.

with two water molecules, H_6O_{4w} with three, and so forth. The two hydration structures in the O^0 have maxima near those of the SPC/E water, and the H_3O_2 in H^0 has the maximum around 165° .

C. Hydrogen bonds

We obtained the distribution of hydrogen bonds between the OH^0 and the water and water-water molecules. Figure 5 shows a comparison between the water-water and OH^0 -water hydrogen-bond distributions. The OH^0 establishes one hydrogen bond 43% of the time, and it establishes two hydrogen bonds with the water molecules that surround it 6.5% of the time. During 50.5% of the time the OH^0 remains without establishing hydrogen bonds with the solvent.

Figure 6 shows a comparison of hydrogen-bond distributions where the OH^0 acts as donor (H^0) and as acceptor (O^0). As acceptor, the OH^0 establishes one hydrogen bond only 11% of the time, while for the rest of the time it does not establish hydrogen bonds. On the other hand, the OH^0 acts as donor establishing one hydrogen bond 42% of the time. These calculations allow us to deduce that the OH^0 does not adapt to the structure of the solvent, in spite of the strong hydration structure existent around the H^0 .

D. Lifetimes

We computed the lifetimes of the hydration structures on the two OH^0 and the water atoms. The cut-off radius in the hydration water structures was 2 \AA . Table II shows the results. On the OH^0 , the hydration structures have lifetimes between 30 and 35 fs. The lifetimes of the water hydration

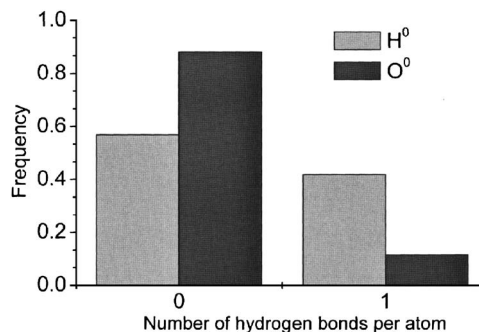


FIG. 6. Hydrogen-bond distributions per atom for the O^0 and for the H^0 (OH^0 as acceptor and donor, respectively).

structures are longer than those that correspond to the OH^0 . The structure with the longest lifetime is H_6O_{3w} .

Using the criteria defined by Samoilov²² for ions, the hydration lifetimes indicate that the OH^0 has a negative hydration. This definition considers the ratio of the water residence time $R = \tau_{\text{molecule}} / \tau_{\text{bulk}}$, where τ_{molecule} is the lifetime of the water molecules in its first hydration shell and τ_{bulk} the lifetime of the water molecules in the bulk. When $R > 0$ it is defined as the positive hydration and for $R < 0$ it is defined as the negative hydration. In our case we have that $\tau_{\text{OH}^0 \text{ structure}} / \tau_{\text{H}_2\text{O structure}} < 1$, then, according to the definition, the hydration of the OH^0 is negative.

E. Diffusion of the OH^0

We obtained $7.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for OH^0 and $2.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for water as diffusion coefficients. The diffusion coefficient of water is not altered by the presence of the OH^0 molecules, in agreement with previous simulation and experimental values.^{19,23}

IV. CONCLUSIONS

We studied a model of the OH^0 molecule in SPC/E water using classical MD. With this study we obtained a group of properties about the hydration and diffusion of the OH^0 molecule.

Among the different hydration structures for the OH^0 molecule that we obtained, the most abundant is that with a water molecule bound to the hydrogen radical (around 88% of the time), and other water molecule bound to the oxygen radical (around 56% of the time).

The low percentage of hydrogen bonds between the OH^0 and the water indicates the small adaptability of this molecule to the structure of the solvent. In the hydrogen bonds between these molecules, the OH^0 acts as donor 42% of the time, and as acceptor only 11% of the time. The $g(r)$ that corresponds to the bond $\text{O}^0 - \text{H}^0 \cdots \text{O}$ has a defined peak at 1.7 Å, and its $P(\cos \phi)$ has a maximum at $\phi = 165^\circ$, which are characteristic of the formation of hydrogen bonds. On the other hand, the formation of the bonds $\text{H}^0 - \text{O}^0 \cdots \text{H}$ is less frequent than that of $\text{O}^0 - \text{H}^0 \cdots \text{O}$. $g_{\text{O}^0\text{O}}(r)$ has a short peak at 2.7 Å the same as $g_{\text{O}^0\text{H}}(r)$ at $r \sim 2$ Å. In the same way, the $P(\cos \phi)$ of the hydration structures on the O^0 does not have very defined peaks compared with that of the H^0 . Then, the total frequency of hydrogen-bond formation on the O^0 is lower than half of the total frequency of hydrogen-bond formation on the H^0 . However, the unequal formation of hydrogen bonds on the O^0 and H^0 does not influence the stability of the respective hydration structures, since the lifetimes of the main hydration structures on the OH^0 are all around 35 fs. In turn, all the lifetimes of the hydration structures on the OH^0 are shorter than those corresponding to the hydration structures of the water molecule. The diffusion coefficient of the OH^0 is higher than that of the water molecule. This fact agrees with the negative hydration of the OH^0 and the absence of hydrogen bonds between the OH^0 and the water 50.5% of the time.

There are important differences between the hydration structures in the O^0 and the oxygen of the $\text{OH}^-(\text{O}^*)$.¹⁷ The

main hydration structures in the O^* are O_3H_5^- (38% of the time) and O_4H_7^- (39% of the time). Their bonds $\text{O}^* - \text{H}$ are nearly in a planar configuration, because their $P(\cos \phi)$ functions have a maximum in $\phi = 96^\circ$ and $\phi = 94^\circ$, respectively. The lifetimes of the O_3H_5^- and O_4H_7^- structures are similar to those of the OH^0 (21 and 32 fs, respectively). However, the OH^- has smaller mobility than the OH^0 , its diffusion coefficient being $5.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. In this way, the RDF of water oxygen atoms around the O^* has a first peak higher than those of the $g_{\text{O}^0\text{O}}(r)$ [Fig. 1(a)].

Our conclusions agree in part with works cited previously. We found that the OH^0 acts preferably as proton donor,^{6,8,13,14} and that it does not adapt to the water structure.¹⁰

The molecular model used and the detailed description of the behavior of the OH^0 provided in this work can be very useful in studying the group of processes in which the hydroxyl radical in water intervenes.

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