

Ab Initio Simulation of Rotational Dynamics of Solvated Ammonium Ion in Water

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Abstract: We have performed an ab initio molecular dynamics simulation of the rotational dynamics of NH_4^+ ion in water. This work was motivated by the experimental evidence that the solvated NH_4^+ rotates rather fast, despite the expected formation of strong hydrogen bonds with water. We find that NH_4^+ is on average coordinated with five water molecules. Four water molecules form a long-lived tetrahedral cage around the ion, each molecule being hydrogen-bonded with one proton of NH_4^+ . The fifth water molecule is much more mobile and occasionally exchanges with one of the four molecules in the tetrahedral cage. The hydrogen bonding of NH_4^+ with water is strong enough to prevent the free rotation of the ion, which instead tumbles in a sequence of discontinuous rotational jumps associated with the exchange of two water molecules in the tetrahedral cage. The simulated rotational dynamics is consistent with nuclear magnetic resonance data and encourages the use of ab initio simulations to describe the solvation of ions in water.

Introduction

The solvation structure and dynamics of ions in water play an important role in many chemical and biological processes. In particular, ammonium ion (NH_4^+) in water has been studied extensively, because it is an important chemical species and provides a simple model for solvated amides.^{1–10} Renewed interest in this system has been provoked by recent nuclear magnetic resonance (NMR) measurements^{1,2} that indicate that the solvated ammonium ion rotates rather fast, despite the expected formation of strong hydrogen bonds with water molecules. Several rotational mechanisms have been proposed based on ab initio calculations of ammonium in water clusters,⁸ molecular dynamics,^{9,10} and Monte Carlo⁷ classical simulations of ammonium in liquid water. Although some of the classical simulations^{4,5,9} show a fast diffusive rotational motion, no consensus has been achieved so far on even the structure of the first solvation shell of ammonium, which is a necessary prerequisite to the understanding of the rotational mechanism. In this paper we present the results of a density functional-based Car–Parrinello¹¹ molecular dynamics simulation of the ammonium ion in water, which provides crucial insights into

the rotational dynamics of the ion and the structure of its solvation shell. In recent years Car–Parrinello simulations have been applied to the study of several ions and molecules in water, such as hydronium,¹² hydroxyl,¹² Be^{2+} ,¹³ SO_3^- ,^{14,15} K^+ ,¹⁶ and glucose.¹⁷

We find that NH_4^+ in water is on average coordinated with five ($n_c = 5.3$) water molecules in the first solvation shell. Four water molecules form a long-lived tetrahedral cage around the ion, each molecule being hydrogen-bonded with one proton of NH_4^+ . The fifth water molecule is mainly localized at the center of the tetrahedral faces defined by the other four molecules. Occasionally an exchange occurs between the fifth molecule and one of the four molecules in the tetrahedral cage. The exchange event drives a partial rotation of the ion via the bifurcation of two H-bonds. The hydrogen bonding of ammonium with water is strong enough to prevent the free rotation of the ion, which instead tumbles in a sequence of discontinuous rotational jumps associated with the exchange of two water molecules in the tetrahedral cage. The picture of the rotational dynamics and the estimated frequency of the sudden reorientations that emerge from the simulation are consistent with the NMR data and encourage the use of Car–Parrinello molecular dynamics to describe the solvation of ions in water.

Computational Method

We performed ab initio molecular dynamics simulations using the Car–Parrinello scheme.^{11,18,19} Our approach is based on density functional theory within the local density approximation of the

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exchange–correlation functional augmented by the gradient corrections proposed by Becke²⁰ and Lee et al.²¹ (BLYP), which has been shown to provide the best description of the hydrogen bond in water.²² Only valence electrons are treated explicitly and electron–ion interactions are described by norm-conserving pseudopotentials generated according to the Troullier and Martins procedure.²³ The reliability of our framework in describing the solvation of NH_4^+ was previously checked on small $\text{NH}_4^+(\text{H}_2\text{O})_n$ clusters ($n = 1-5$).²⁴ Dynamical properties of liquid water such as self-diffusion coefficient and rotational correlation time have been reproduced as well within our framework.²² We used a cubic supercell ($a = 12.42 \text{ \AA}$) containing 63 water molecules and one ammonium ion with periodic boundary conditions. The supercell volume was chosen so as to reproduce the density of water at normal conditions and the experimental value of the apparent molar volume of ammonium ion in water at infinite dilution.

Kohn–Sham orbitals have the periodicity of the supercell (only Γ point used in the Brillouin zone integration) and are expanded in plane waves up to a kinetic energy cutoff of 70 ry. In the dynamical simulation a fictitious electronic mass of 1100 a.u. and a time step of 0.17 fs have been used. After an equilibration time of 5 ps at room temperature, statistical averages were collected from a microcanonical run 10 ps long. To increase the simulation time step we substituted hydrogen with deuterium. This choice does not affect the structural properties of the solvation shell. Experimental data on the isotope effects show that the ratio between the rotational relaxation time of NH_4^+ and ND_4^+ is $\sqrt{2}$, which could be related in a first approximation to the change in the moment of inertia.^{1,2} Possible finite size effects due to the relatively small simulation cell have been checked via classical molecular dynamics simulations using the empirical potentials of ref 4. The comparison of the N–O pair correlation functions $[g_{\text{NO}}(r)]$ obtained from classical simulations of 64 and 729 molecules shows that the size of the cell chosen in the ab initio simulation is large enough to reproduce correctly the second solvation shell of ammonium. Beyond the second solvation shell the $g_{\text{NO}}(r)$ is structureless.

Results and Discussion

The solvation shell of the ammonium ion can be described by the set of simulated pair correlation functions in Figure 1. The first solvation shell is formed on average by about five water molecules. To be more precise, the coordination number is found to be $n_c = 5.3$ when $g_{\text{NO}}(r)$ is integrated up to the first minimum. The coordination number of each deuterium of ND_4^+ is 1.0, obtained by integrating $g_{\text{D}^*\text{O}}(r)$ up to the first minimum, where D^* refers to the deuterium atoms of ammonium. In fact, four molecules in the first solvation shell are H-bonded with the deuterium atoms of ammonium, forming a long-lived tetrahedral cage. The tetrahedral cage lasts up to 4 ps before an exchange with outer molecules takes place. The tetrahedral cage around the ammonium ion is very similar to the structure of the isolated $\text{ND}_4^+(\text{D}_2\text{O})_4$ cluster. The internal structure of ND_4^+ in solution does not change appreciably with respect to the isolated ion.²⁴ The distribution function $P[\cos(\theta)]$ of the angle θ between the geometric dipole vector of the molecules in the tetrahedral cage and the relative D^*O bonds is reported in Figure

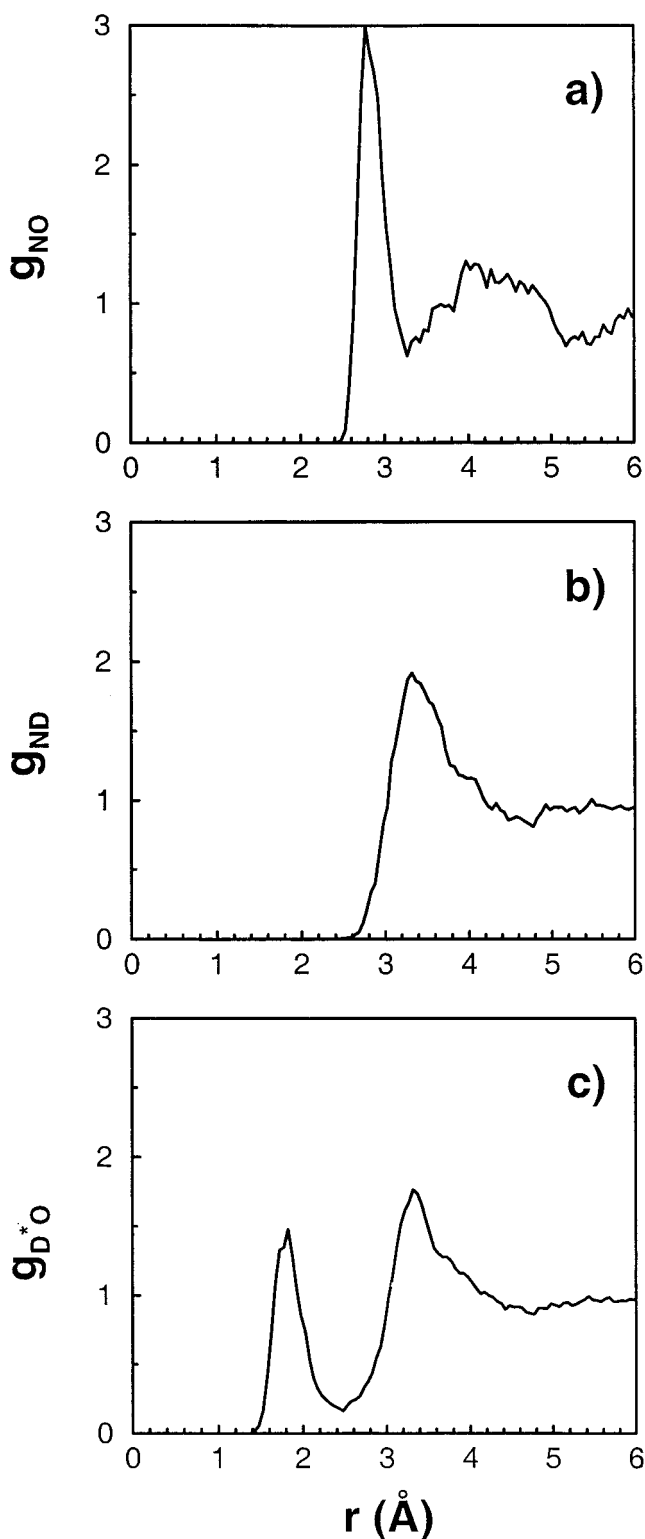


Figure 1. Simulated radial pair correlation function for (a) nitrogen–oxygen; (b) nitrogen–deuterium of the deuterium atoms in water molecules; (c) deuterium–oxygen of the deuterium atoms in the ammonium ion, labeled as D^* . Data are collected over a microcanonical run 10 ps long.]

2. $P[\cos(\theta)]$ has a maximum at $\theta_m \sim 20^\circ$. Conversely, in the isolated $\text{ND}_4^+(\text{D}_2\text{O})_4$ cluster the geometric dipole vector is aligned with the D^*O bond and θ_m is 0° . The rotation of the molecules in the first solvation shell with respect to the isolated clusters is due to the H-bonding with outer molecules in the liquid.

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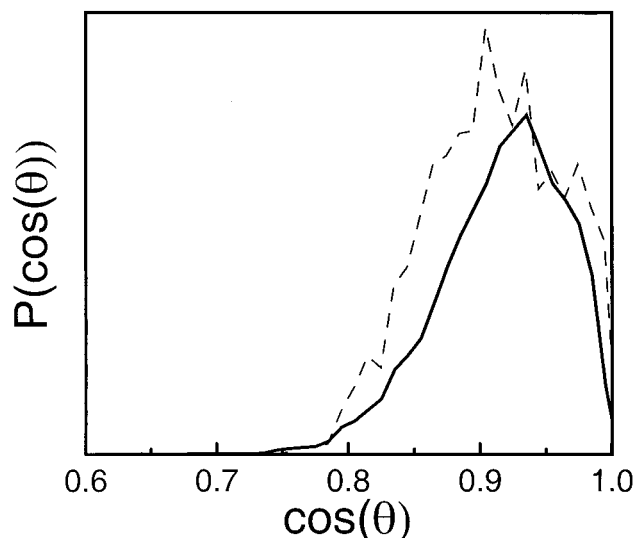


Figure 2. Angular distribution of the dipole moment of the four water molecules H-bonded with the ammonium ion with respect to the relative D*O bonds, where D* indicates deuterium atoms of ammonium. The solid line is obtained by averaging over the whole simulation run 10 ps long. The dashed line is obtained by averaging over a shorter interval of 4 ps, in which no exchange takes place between the water molecules in the tetrahedral solvation shell.]

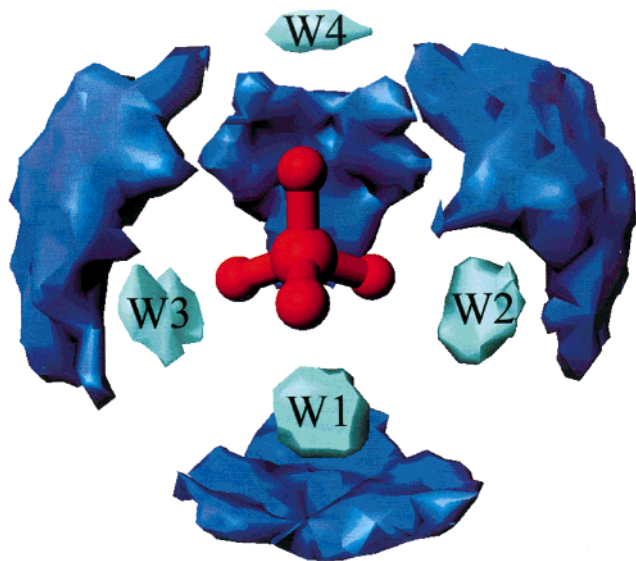


Figure 3. Distribution of the position of the fifth water molecule in the first solvation shell of ammonium. The other four water molecules in the first solvation shell are H-bonded to the four deuterium atoms of ND_4^+ . Their average position is denoted by W_i , $i = 1, 4$.

Besides the well-defined tetrahedral cage of H-bonded water molecules, a fifth water molecule lies within the first solvation shell. This latter molecule is much more mobile than the four water molecules in the tetrahedral cage; it changes identity several times in our simulation run and visits all the faces of the tetrahedral cage. The distribution of the position of the fifth water molecule is shown in Figure 3.²⁵ It tends to occupy the center of the tetrahedral faces defined by the four water molecules H-bonded with ammonium. The presence of the fifth water molecule at the center of one tetrahedral face induces a widening of the occupied face and a shrinking of the other empty

(25) The fifth water molecule is defined as the water molecule closer to the nitrogen that is left in the first solvation shell once the four water molecules in the tetrahedral geometry (i.e., closest to the four protons of ammonium) have been excluded.

faces. Once a water molecule is present at the tetrahedral face defined, for instance, by the water molecules W_1 , W_2 , and W_3 in Figure 3, these latter water molecules are pushed outward and upward in such a way as to widen the tetrahedral edges defined by these molecules. As a result the other edges of the tetrahedron shrink, preventing access to other water molecules at the center of the other tetrahedral faces.²⁶ As a consequence the average coordination number of ammonium is close to five. Our simulation run is too short to give a very precise number for the residence time of the water molecules in the first solvation shell. However, our data clearly show that the residence time of the fifth water molecule is much shorter than the residence time of water molecules in the tetrahedral shell. We computed the residence time according to the definition given by Impey et al.²⁷ The latter authors define an average coordination number as

$$n(t) = \frac{1}{N} \sum_{n=1}^N \sum_j P_j(t_n, t) \quad (1)$$

where the first sum is over N ionic configurations at times t_n and the index j runs over all the water molecules in the simulation box. The function $P_j(t_n, t)$ is equal to 1 if the j th water molecule belongs to the solvation shell both at times t_n and $t_n + t$ and zero otherwise (we have chosen $t^* = 0$ in the notation of ref 27). At larger times, $n(t)$ decays exponentially as $e^{-t/\tau}$, where τ is by definition the residence time. We obtained $\tau \sim 4$ ps for the molecules in the tetrahedral shell and $\tau \sim 0.08$ ps for the fifth water molecule.²⁵ Although the value of ~ 4 ps is not reliable if obtained by averaging over a run as short as 10 ps, the comparison of the residence time of the tetrahedral and fifth water molecules does give valuable information on the different mobilities of the two types of molecules in the first solvation shell. The fifth water molecule exchanges with water molecules in the second solvation shell, as we explicitly see in the simulation. However, the exchange time is longer than the residence time $\tau \sim 0.08$ ps as given above. In fact, in the definition of the residence time, events are also included where the fifth water molecule leaves the first solvation shell for a while, but then comes back before being replaced by a water molecule of the second shell.

The coordination number of NH_4^+ in water is very close to the coordination number of water in water ($n_c = 4.5$ theory,¹⁴ $n_c = 5.2$ exp.²⁸). However, there are important differences in the structure of the solvation shells of water and ammonium. In the solvation shell of water (see for instance ref 29), the tetrahedral geometry of the solvation shell is much less defined than in NH_4^+ . Furthermore, ammonium ion is a donor of four H-bonds, whereas water is an acceptor of two H-bonds and a donor of two other H-bonds. Consequently the orientation of the water molecules in the nearly tetrahedral solvation shell of water and ammonium is different. Moreover, the position of the fifth water molecule in the first solvation shell of water as given in ref 29 is different from the fifth water molecule of the ammonium solvation shell given in Figure 3.

Experimental data on the structure of the solvation shell of ND_4^+ ion are available from neutron³ and X-ray⁶ diffraction

(26) In a sampled configuration with a fifth water molecule at the center of the face defined by W_1 , W_2 , W_3 in Figure 3, the water-water distances in the tetrahedral cage are as follows (cfr. Figure 3): $W_1-W_2 = 4.6$ Å, $W_2-W_3 = 5.2$ Å, $W_1-W_3 = 5.4$ Å, whereas the edges of the other faces are $W_3-W_4 = 4.7$ Å, $W_2-W_4 = 3.6$ Å, $W_1-W_4 = 4.5$ Å.

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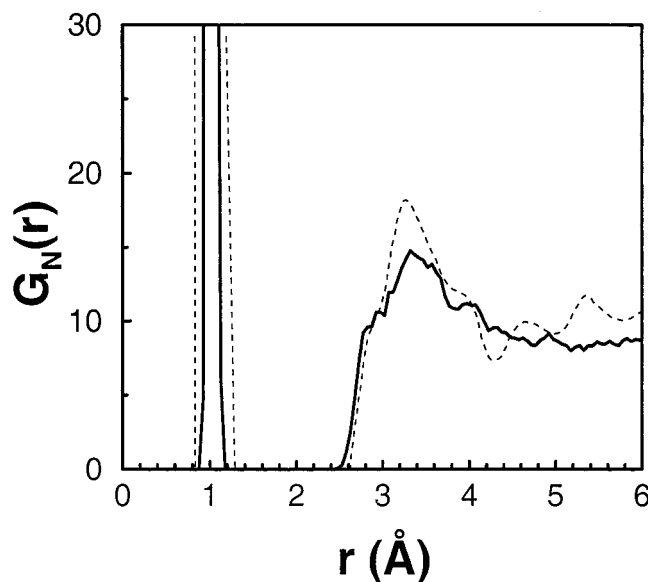


Figure 4. The N–water total distribution function [$G_N(r)$ of eq 1 in the text] is shown as a solid line. The neutron-diffraction data of ref 3 are shown for comparison (dashed line).

spectroscopy. The most reliable experimental data come from first-order neutron diffraction measurements on isotopically substituted samples by Hewish and Neilson.³ The latter authors have been able to measure by neutron diffraction the following correlation function:

$$G_N(r) = 0.00260 g_{NO}(r) + 0.00716 g_{ND}(r) + 0.00043 g_{NCl}(r) + 0.00035 g_{NN}(r) - 0.01038$$

where D here denotes all deuterium atoms of ammonium and water molecules. This is obtained from the difference of the total scattering intensities of two 5 *m* heavy water solutions of ND₄Cl with different amount of ¹⁴N and ¹⁵N isotopes. The numerical values in eq 2 (in barn) are given by the ionic concentrations and the neutron scattering length of the different isotopes used.³ We calculated the $G_N(r)$ correlation function in eq 2 by using our simulated $g_{NO}(r)$ and $g_{ND}(r)$ and by neglecting $g_{NCl}(r)$ and $g_{NN}(r)$, which have a smaller numerical prefactor in eq 2. The theoretical $G_N(r)$ is compared with the experimental $G_N(r)$ in Figure 4. The peak at $r \sim 1.0$ Å is due to intramolecular deuterium. The shoulders at ~ 2.8 Å and ~ 4.0 Å, and the peak at ~ 3.2 Å are well reproduced by our calculation. They are due to the first and second peaks of the $g_{NO}(r)$ correlation function and to the first peak of the $g_{ND}(r)$ correlation function, respectively. The sharp minimum at ~ 4.4 Å and the additional outer peaks in the experimental data are not reproduced by our calculation. These latter features might be due to the large concentration of the experimental solution (5 *m*, i.e., one ammonium ion every 10 water molecules). At the experimental concentration the second solvation shell is shared between neighboring solute ions. Note also that the minimum in the experimental $G_N(r)$ at ~ 4.4 Å is beyond the first minimum of the $g_{NO}(r)$ correlation function, and the coordination number given in ref 3 and obtained by integration $G_N(r)$ up to 4.4 Å is likely to include both the molecules in the first solvation shell and most of the molecules in the second shell.

Actually, as apparent from the comparison of the total pair correlation function in Figure 4 with the individual correlation functions in Figure 1, the experimental difficulties in the determination of the coordination number of ammonium is two-fold. In fact, besides the aforementioned problems due to the

high concentration of the experimental solution, the overlap between the peak of $g_{ND}(r)$ and the first minimum of $g_{NO}(r)$ prevents the identification of the first solvation shell in the total scattering function $G_N(r)$ measured experimentally (cfr. eq 2). A definitive experimental determination of the solvation shell of ammonium would require second-order neutron diffraction measurements using different isotopes of hydrogen as well,³¹ which could isolate the contributions of $g_{NO}(r)$ and $g_{ND}(r)$. More dilute solution would also be required to minimize solute–solute interactions. These experiments have not been performed so far, and our ab initio simulation attempts to fill in the gap.

Among the previous simulations (Monte Carlo and molecular dynamics) using empirical potential, the work of Jorgensen and Gao⁷ predicts a coordination number $n_c = 5.2$, very close to our result, whereas other authors^{4,10} find a coordination number in the range $n_c = 8.1$ – 8.4 . However, the Jorgensen and Gao definition of n_c is different from ours. They define n_c as four times the coordination of the ammonium hydrogen atoms. By using the definition used by Jorgensen and Gao, we obtain $n_c = 4.0$, which indicates a significant discrepancy between their solvation structure and ours. In the procedure of Jorgensen and Gao our fifth water is not included because it stays away from the ammonium deuterium while coming close to the N atom.³⁰ Our definition of n_c as the integral over the first peak in $g_{NO}(r)$ appears to better reflect the properties of the coordination shell. We conclude that our results are at variance with exiting simulations based on empirical potentials. The potentials so far used have clear limitations, such as the use of rigid water molecules or of two-body only nitrogen–water interaction, but it is difficult to pinpoint where the major problems lie. The construction of new improved empirical potentials could benefit from the data provided by our ab initio simulation.

The present simulation provides crucial insights into the dynamics of the solvation shell and the rotational properties of ammonium. As already anticipated, NMR measurements have been interpreted by assigning a rather fast rotation of ammonium in water.^{1,2} In fact, the measured rotational correlation time τ_c of ammonium is 1.1 ps. This is the time required for the NH₄⁺ to rotate within its solvation shell by an angle of 33° about any axis. The rotation of ND₄⁺ is retarded by a factor $\sqrt{2}$, as expected from the increased moment of inertia.¹

The analysis of the orientation in space of ammonium in our simulation reveals that the rotational dynamics of the ion is very far from that expected for a nearly free rotator. The ion mainly librates around a fixed orientation in space, but occasionally undergoes sudden reorientational jumps. However, between successive jumps the molecular librations are quite large and the deviations from the mean angle are as large as 20°.

We find that the sudden reorientation of the ammonium ion is associated with the exchange of two molecules in the tetrahedral solvation cage. Although the ND₄⁺(D₂O)₄ cluster is rather stable, one water molecule in the cluster occasionally exchanges with the fifth water molecule of the first solvation shell. In this process the fifth water molecule moves from its most probable position at the center of the tetrahedral face to the face corner, closer to one of the H-bonded water molecules in the tetrahedral cage. At this point the D*O bond bifurcates

(30) A fifth water molecule at the center of the tetrahedral face and 3.2 Å from the N atom [minimum of the $g_{NO}(r)$] is still 3.6 Å from the hydrogen atoms of ammonium. This distance is much above the first minimum of the $g_{D^*O}(r)$ pair correlation function. Therefore the coordination numbers obtained by integrating $g_{NO}(r)$ or by multiplying by four the coordination number of hydrogen in ammonium [as obtained by integrating $g_{D^*O}(r)$] are different in our case.

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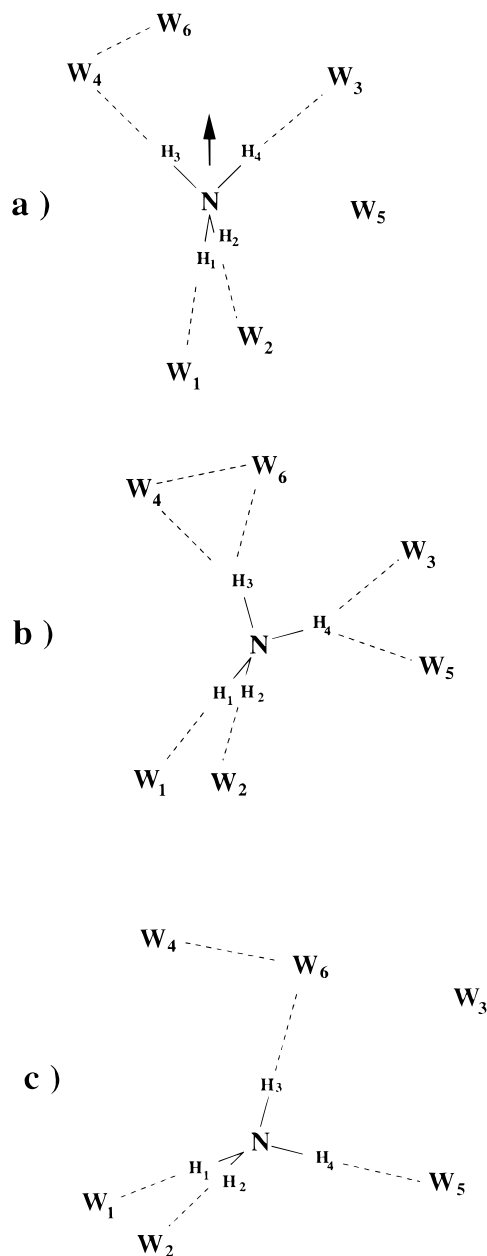


Figure 5. Sketch of the mechanism of ND_4^+ rotation as it emerged from the simulation. The position of the six water molecules involved in the rotational process is depicted as W_i , $i = 1, 6$. (a) Initial configuration ($t = 6.0$ ps): the four molecules W_1 , W_2 , W_3 , and W_4 form the tetrahedral solvation cage. W_5 is the fifth water molecule in the first solvation shell. W_6 belongs to the second solvation shell and is H-bonded to W_4 . (b) Intermediate configuration ($t = 6.7$ ps): the ammonium is partially rotated along a rotational axis perpendicular to the plane of the figure (z -axis). The rotational axis is mainly parallel to the line joining molecules W_1 and W_2 , which keep their H-bonding with ammonium. Two H-bonds are bifurcated. (c) Final configuration ($t = 7.5$ ps): the rotational jump is completed. Two water molecules in the tetrahedral cage are exchanged with two outer water molecules (W_3 exchanged with W_5 and W_4 exchanged with W_6). W_1 and W_2 followed the rotation of ammonium, keeping their H-bonding with the ion. The time scale corresponds to the rotational event illustrated in Figure 6. The vector originating from N in panel (a) corresponds to the sum of the two vectors $\text{NH}_3 + \text{NH}_4$; it is the geometric dipole due to the N, H_3 , and H_4 atoms and defines the rotational angle of Figure 6. Our intermediate configuration (panel b) does not correspond to any of the clusters proposed in ref 8 as a possible saddle point configuration of the rotational mechanism.]

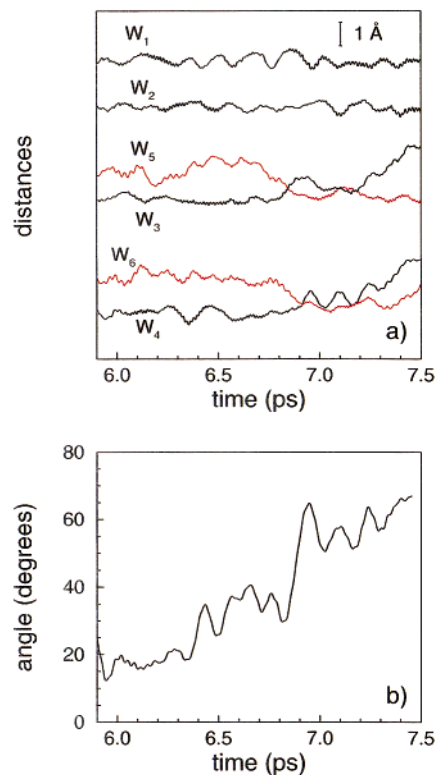


Figure 6. (a) Plot of the distance of the water molecules of Figure 5 from the nearest deuterium atoms of ammonium during one rotational event. The labels W_i , $i = 1-6$, are the same as in Figure 5. (b) Angle of rotation ϕ as a function of time. ϕ is defined as the angle between the instantaneous and the initial orientation of the vector $\text{NH}_3 + \text{NH}_4$ shown in Figure 5, which is nearly perpendicular to the rotational axis. The rotational jump is clearly associated with the exchange of two water molecules in the tetrahedral cage. To integrate out the fast and large librational modes, we smoothed $\phi(t)$ over a time interval of 80 fs.

and coordinates both molecules. Then the former fifth water molecule takes the place of the molecule previously bonded in the tetrahedral cage. The latter is in turn expelled from the tetrahedral cage. The exchange drives a partial rotation of the ammonium ion. A cartoon of the mechanism of rotation as it emerged in the simulation is sketched in Figure 5. In the simulation, 10 ps long, we saw three rotational jumps, all associated with the exchange of two water molecules in the tetrahedral cage, as shown in Figure 5. The four water molecules labeled W_1 , W_2 , W_3 , and W_4 in Figure 5 initially form the tetrahedral solvation cage. The rotational axis is perpendicular to the plane of Figure 5. It is mainly parallel to the axis joining the two water molecules in the tetrahedral cage (W_1 and W_2), which keep their H-bonding with the ammonium ion during the rotation. Although the rotational jump is initiated by the exchange of the fifth water molecule (W_5 , which exchanges with W_3 in Figure 5), another outer water molecule (W_6) comes into play in the process. This sixth water molecule belongs to the second solvation shell but it is H-bonded to one water molecule in the first tetrahedral solvation cage (W_4 in Figure 5). Also, these two molecules (W_4 and W_6 in Figure 5) exchange their positions during the rotation, keeping each other H-bonded. Finally, just two H-bonds are bifurcated and two water molecules in the tetrahedral cage are exchanged with outer molecules. The rotational mechanism described above is demonstrated by the analysis of the simulated atomic trajectories across one rotational event reported in Figure 6. The latter figure shows the distance of the six water molecules involved in the rotational event (cf. Figure 5) from the nearest deuterium atom

of ND_4^+ . The exchange of molecules in the tetrahedral cage (W_4 with W_6 and W_3 with W_5) is clearly coincident with a jump in the rotational angle ϕ reported in Figure 6b.

It is of interest to compare our results with those of gas-phase calculations and experiments. Recent gas-phase experiments backed by ab initio calculations ascribe stability of four, five, and six water molecule clusters to structures where there is a core of four water molecules tetrahedrally bound to the ammonium ion, whereas the additional ones are hydrogen-bonded to form the initial stages of a second solvation shell. Therefore these structures are not as a good model for the liquid-state solvation where the presence of a fifth water in the first solvation shell plays a crucial role. The possible relevance of a fifth water molecule for the rotational mechanism was first hypothesized in refs 1 and 8, in which the availability of additional water molecules is deemed crucial to allow the ammonium ion to rotate without breaking three H-bonds. However, the transition energy barrier came out to be too large because in their calculation⁸ the solvation shell is kept fixed while the ammonium rotates. A rotation of ammonium in a rigid solvation cage would imply the bifurcation of three H-bonds and the presence of water molecules simultaneously coordinated with two deuterium atoms of ammonium. No such water molecules are found in our simulation. In fact, the solvation shell is rather flexible and allows for the two water molecules W_1 and W_2 in Figure 5 to keep their hydrogen bonding with the ion during the rotation, leading to a much faster rotational dynamics.

The number of reorientational events seen in the simulation is consistent with the rotational correlation time measured by NMR. In our simulation, 10 ps long, we saw three rotational jumps of amplitude $\sim 60^\circ$. This provides an estimate of $\tau_c \sim$

1.9, close to the measured value ($\tau_c \sim 1.5$ ps for $\text{ND}_4^{+1,2}$). This good agreement is partially accidental, due to the limited statistical accuracy of the relatively short simulation run. Nevertheless, our results provide a reasonable estimate of τ_c , which gives us confidence in the reliability of the rotational mechanism observed in the simulation. In the process described in Figure 5, the rate-limiting step for the rotation is controlled by the dynamics of the fifth water in the solvation shell. Therefore, it is the dynamics of the exchange process that determines the activation energy for the rotation as measured experimentally from the temperature dependence of τ_c ($E_A = 2.8$ kcal/mol). A much lower estimate of the rotational barrier ($E_A = 1.6$ kcal/mol) has been provided in ref 1 by comparing the measured τ_c with the value expected for a free rotor dynamics. The inconsistency between the two estimated activation energies has been attributed² to the temperature promotion of particular, undefined conformations of the solvation shell that favor the rotation. According to our picture, the attempt frequency for rotation is not the frequency of the free rotor, but is determined by an interplay between the librational motion of the ion³² and the motion of the fifth water molecule. Therefore, it is not surprising that the activation energies estimated in the two different ways described above do not coincide.

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(32) The librational frequency in our simulation is $r \sim 10$ THz, whereas the rotational frequency of the ND_4^+ free rotor at room temperature is ~ 1 THz.