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Simulation Study on the Structure and Dynamics of Water in Sodium Tetrafluoroborate/Water

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(Dated: Received on May 18, 2009; Accepted on July 15, 2009)

The microstructure, IR spectrum, as well as rotation dynamics of water molecule in sodium tetrafluoroborate (NaBF_4)/water mixture at room temperatures were studied with molecular dynamics simulation. Different concentrations of water (6.25%, 25.0%, 50.0%, 75.0%, 90.0%, and 99.6%) in NaBF_4 /water mixture were simulated to understand the structure and dynamics. It was shown that water molecules tend to be isolated from each other in mixtures with more ions than water molecules in both liquids. With increase of the molar fraction of water in the mixture, the rotation bands and the bending bands of water display red shift whereas the O–H stretch bands show blue shift, and the decay of the reorientation correlation function becomes slower. This suggests that the molecules are hindered and their motions are difficult and slow, due to the hydrogen-bond interactions and the inharmonic interactions between the inter- or intra-molecular modes.

Key words: Sodium tetrafluoroborate/water mixture, Structure and dynamics, IR spectrum, Reorientation dynamics, Time correlation function, Molecular dynamics simulation

I. INTRODUCTION

The solvation of ions in water is of fundamental importance in chemistry, physics, and biology [1–6]. The existence of ions to water has a dramatic effect on the structure of the liquid which leads to a severe disruption of the hydrogen-bonded structure of the liquid and to the formation of solvation shells [4–6]. Hydrogen bond structure and dynamics play very important roles in solvation processes of many chemical and biochemical reactions [7–9]. As many chemical and biochemical reactions occur in ion aqueous solution, it is important to understand the structural and dynamic properties of solvation shells. Over the last decades, many experimental efforts [4–13] such as ultrafast spectroscopy [10,11], neutron and X-ray diffraction techniques [12,13] have been used to reveal the structure and dynamics of ions or salts such as NaX , LiX , and CsX (X: F, Cl, Br, and I) in water. However, it is difficult to obtain the detailed microscopic structure and dynamics of inner solvation shells directly. There are two often encountered problems in these studies, one is that the intrinsic measuring times are long compared to the exchange time of water between the hydration shells and the bulk, the other is that it is difficult to distinguish the dynamics of the solvation shells from the bulk liquid [14]. As a

result, nowadays, most of the dynamical information of ionic hydration shells does not come from experimental studies but stems from molecular dynamics simulations [1–6]. Up to now, theoretical studies have mainly focused on solvation of cations [14,15] and less attention has been paid on anions [1–6,16] and the lifetimes of solvation shells. Whether and how much influence an ion has beyond the hydration shell(s) is still an open question.

Over the last decade, the tetrafluoroborate salts have been widely used to synthesis the ionic liquids containing tetrafluoroborate anions (BF_4^-). Ionic liquids (ILs), liquids at ambient temperature, are completely composed of organic cations and inorganic/organic anions [17]. They have many attractive properties, such as low melting points, negligible vapor pressure, non-volatile, nonflammable, and wide electrochemical windows, and they have been widely applied to many fields such as organic synthesis, catalysts, materials preparation, chemical engineering, extraction, and electrodeposition of metals [18–20]. However, physicochemical properties of these liquids have not been reported systematically in the literature because of the impurity in ionic liquid. Water is the most problematic impurity for ionic liquids. It is known that most ionic liquids can absorb significant amount of water from the air, and water can react with some ionic liquids. The presence of small amount of water in ionic liquids may largely affect the reaction rate and the selectivity of the reactions taken into, and also has a large effect on their thermodynamics and solvent properties such as polarity, viscosity, and

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conductivity [21–26]. The content of water in various ionic liquids may be strongly influenced by the nature of the cation and anion. Thus understanding the structure, interactions, and dynamics properties of water or other small impure molecules in ionic liquids can help us control or remove these impure species.

Over recent years, the spectroscopy measurement [21–26] and computer simulations [27–32] have been used to reveal the structure and dynamics of ionic liquids/water mixture, such as [Bmim]Cl/water, [Bmim]BF₄/water, [Bmim]PF₆/water, etc. However, the molecular states, dynamics, and the origins of solubility of water in ionic liquid are not clear yet. It was reported that the interactions between water and ionic liquids are mainly determined by the interactions of the water with the anion of the ionic liquids [33]. To elucidate the interactions and dynamics clearly, in this work, the structure and dynamics of water in NaBF₄/water mixture at room temperature were studied with molecular dynamics simulation. Results offer an explanation for available experimental findings and make predictions for the experimental verifications.

II. METHODOLOGY AND SIMULATION DETAILS

The BF₄⁻/water mixture considered in this work has molar fractions of water $x_1=6.25\%$, 25.0% , 50.0% , 75.0% , 90.0% , and 99.6% , the numbers of molecules and the density used in each simulation depending on the 6 mixture are given in Table I, where the molal fraction x is computed by treating the Na⁺ and BF₄⁻ as a single unit.

TABLE I System sizes for different run.

x_1	N_1 (water)	N_2 (Na ⁺ =BF ₄ ⁻)	ρ /(g/cm ³)
6.25%	16	240	0.999758
25.0%	64	192	0.999439
50.0%	128	128	0.999222
75.0%	192	64	0.999014
90.0%	218	38	0.998912
99.6%	255	1	0.998803

A. Methodology

The common method for the determination of the infrared spectrum (IR) is based on the calculation of velocity-velocity time correlation functions $C_a(t)$ of the atomic velocity v_a of the molecules during the molecular dynamics simulations, namely,

$$C_a(t) = \frac{\langle v_a(0)v_a(t) \rangle}{\langle v_a^2(0) \rangle} \quad (1)$$

where $\langle \rangle$ is ensemble average. Then, the IR spectra can be calculated as the cosine Fourier transform of the corresponding velocity-velocity time correlation functions,

$$I(\omega) \propto \int_0^\infty \cos(\omega t) C_a(t) dt \quad (2)$$

This method has been widely and successfully applied to obtain separately the distribution of frequencies corresponding to the motion of atoms that contributions to the spectra of the different kinds of inter or intramolecular motions cannot be distinguished [34,35].

Molecular reorientation motions in liquids are usually analyzed through the time correlation functions [36,37]

$$C_l^\alpha(t) = \langle P_l(\vec{u}^\alpha(t)\vec{u}^\alpha(0)) \rangle \quad (3)$$

where P_l is the l th Legendre polynomial and \vec{u}^α is a unit vector along a given molecular direction, and the angular brackets denote an ensemble average. $C_l^\alpha(t)$ indicates how a given molecular direction changes its orientation in time and can be related to the dielectric relaxation and NMR experiments, for example, $C_1^\alpha(t)$ is directly related to dielectric relaxation measurements, whereas $C_2^\alpha(t)$ is related to dipolar relaxation NMR experiments [37], respectively. Rotational correlation times τ_l^α can be obtained by the time integral of the rotational time correlation function:

$$\begin{aligned} \tau_l^\alpha &= \int_0^\infty C_l^\alpha(t) dt \\ &= \int_0^\infty \langle P_l(\vec{u}^\alpha(t)\vec{u}^\alpha(0)) \rangle dt \end{aligned} \quad (4)$$

In this work, the unit vectors $\vec{u}^{\text{O-H}}$ along with the O–H axis which can be measured by ¹⁷O–¹H dipolar relaxation in NMR experiments, and $\vec{u}^{\text{H-H}}$ along with the H–H directions which can be measured by ¹H–¹H dipolar relaxation in NMR experiments were used to calculate reorientation correlation function and reorientational time.

B. Potential energy surface

The force field parameters of water molecules, are used the modified SPC/E model [38], which the intramolecular potential is given by [39,40]:

$$\begin{aligned} V = D_0 \left\{ [1 - \exp(-\beta\Delta r_1)]^2 + [1 - \exp(-\beta\Delta r_2)]^2 \right\} + \\ \frac{k_\alpha}{2} r_e^2 \Delta\alpha^2 + k_{r\alpha} r_e \Delta\alpha (\Delta r_1 + \Delta r_2) + \\ k_{rr'} (\Delta r_1 \Delta r_2) \end{aligned} \quad (5)$$

where Δr_1 and Δr_2 denote the displacements of the two O–H bond lengths from the equilibrium value r_e and $\Delta\alpha$ is the change of the H–O–H bond angle. The force field parameters in Eq.(5) are taken from Ref.[39],

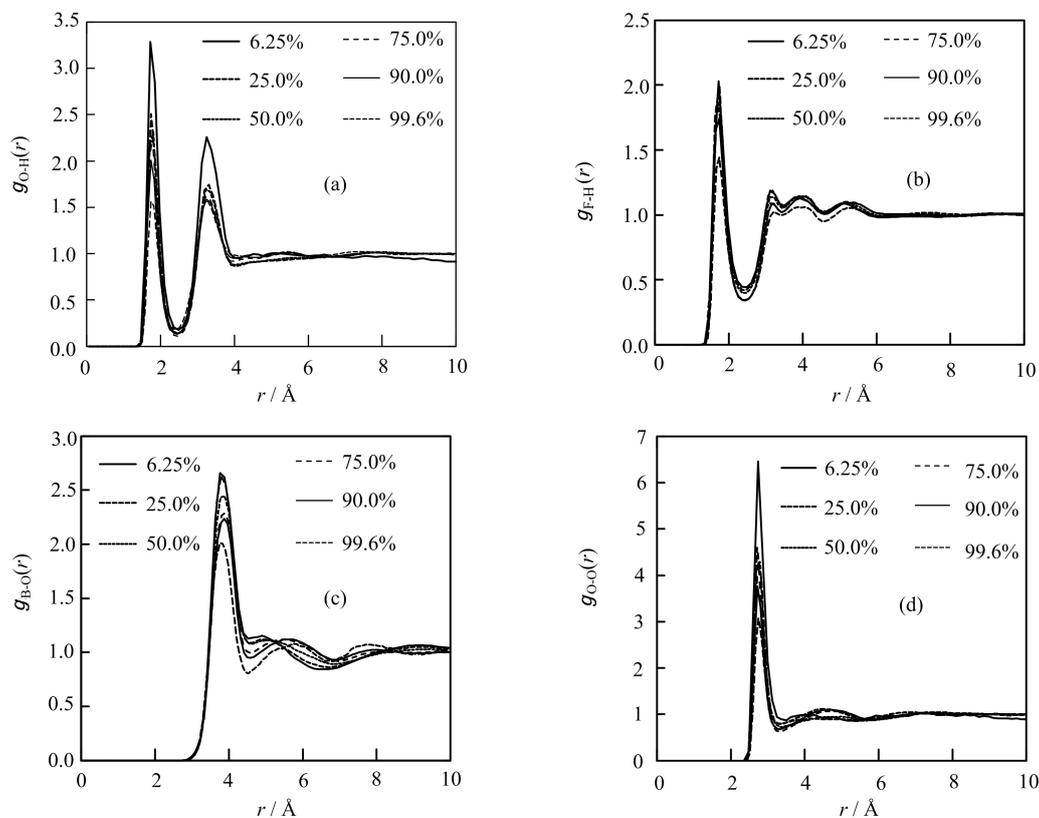


FIG. 1 Radial distribution functions of anions with different concentrations of water.

which has been successfully used to study the structure and dynamics (such as IR spectrum, relaxation dynamics and rotation dynamics) of water molecule in pure water, solution, and the obtained results agree well with experimental results [39,40]. The force field for BF_4^- anions are taken from Ref.[41], which has been widely and successfully used to study the structure thermodynamic and physical properties, dynamics of the ionic liquids formed with BF_4^- anions and other cations [42–44]. The particles interactions of anion-anion and anion-water as well as water-water are simply a pair wise sum of Lennard-Jones (L-J) and Coulomb terms, namely,

$$V^{\text{inter}} = \sum_{i < j} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \right\} \quad (6)$$

where ε and σ are the L-J parameters and r_{ij} denotes the distance between the L-J sites i and j , q_i and q_j are the point charges on site i and j . The L-J parameters and point charges are taken from the original SPC/E model [38] for water, from Ref.[41] for BF_4^- and from Ref.[44] for Na^+ . The L-J parameters of ε_{ij} and σ_{ij} are obtained using the Lorentz-Berthelot mixing rules $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

C. Molecular dynamics simulation details

All molecular dynamics simulations were carried out using an adaptation of the DL_POLY 2.18 program [45]. Cubic periodic boundary conditions are used. The electrostatic forces are treated using the Ewald summation procedure and the internal geometry. The simulation trajectory is propagated by the velocity verlet algorithm with a time step of 1 fs in NVE ensemble. Each system is equilibrated at 300 K by periodically rescaling the velocities of the molecules until the temperature was kept within ± 2 K for 80 ps without further adjustment, after which a production run of 200 ps is performed to calculate the quantities of interest.

III. RESULTS AND DISCUSSION

A. Structure properties

The local structure of a system can be conveniently studied by means of the radial distribution functions. The radial distribution function is a powerful physical tool to describe the microstructure of a system. Figure 1 (a) and (b) show the radial distribution functions $g_{\text{O-H}}(r)$ and $g_{\text{F-H}}(r)$ obtained from the molecular dynamics simulations. Both figures show a first max-

imum at $r=1.85 \text{ \AA}$, which corresponds to the classical hydrogen-bond length. It is indicated that anions are integrated into the water hydrogen-bond network. Furthermore, the sizes of BF_4^- and of water are of the same order of magnitude again enhancing a mixed network. The number of hydrogen-bond between anion and water is slightly less compared to that between two waters, as denoted by the corresponding peak heights in Fig.1 (a) and (b). The strength of the hydrogen-bond between anion and water molecules increases with decreasing of the percentage of water, which indicates that the ionic network exert a directing field on the water molecules, and this field is weakened with increasing $x(\text{H}_2\text{O})$. The second peak in Fig.1(a) is broadened compared to the double peak in Fig.1(b), due to the fact that BF_4^- has three additionally fluorine atom that are not engaged in the hydrogen bonding but nevertheless stabilizing the structural motif.

The radial distribution functions $g_{\text{B-O}}(r)$ and $g_{\text{O-O}}(r)$ are given in Fig.1 (c) and (d). It is shown in Fig.1(c) that the first peaks are sharper and higher in the mixtures with less water, and the region beyond the first peak gradually fill with the increase of the molar fraction of water. In the most dilute solution, one can find that there is also a quantitative change in the position of the second peak. In mixtures with high proportion of water, it is easy to think of the distribution relative to an anion. The growth of the second peak near 4 \AA for BF_4^- come from the establishment of a second shell of water molecules around the anion. It does not occur as most of the water molecules are isolated from each other in solutions with less water. Thus, with the increase of the percentage of water, there is a growing deficit of waters in this region. The first peak represents anions which are hydrogen-bonded to water in the mixtures with few water molecules, while other anions are found beyond 5 \AA from the water molecule. The distribution functions in Fig.1(d) show the buildup of probability of water molecules in the region between 4 and 5 \AA as the number of water clusters, and eventually the network builds up as the molar fraction of water increases in NaBF_4 mixtures. Thus mixtures with low fractions of water have a deficit of both BF_4^- and water molecules in this region.

B. IR spectrum

The normalized hydrogen velocity-velocity time correlation function (Fig.2(a)) of water molecules in the mixtures and corresponding power spectrum (Fig.2(b)) calculated from Eqs.(1) and (2) at each step of the molecular dynamic simulations were given in Fig.2. The corresponding frequencies were given in Table II.

It was shown in Fig.2(a) that the decay becomes slower as the percentage of water increases. From the power spectra $I_{\text{H}}(\omega)$ shown in Fig.2(b), one can see that there are three peaks below 250 cm^{-1} which are consis-

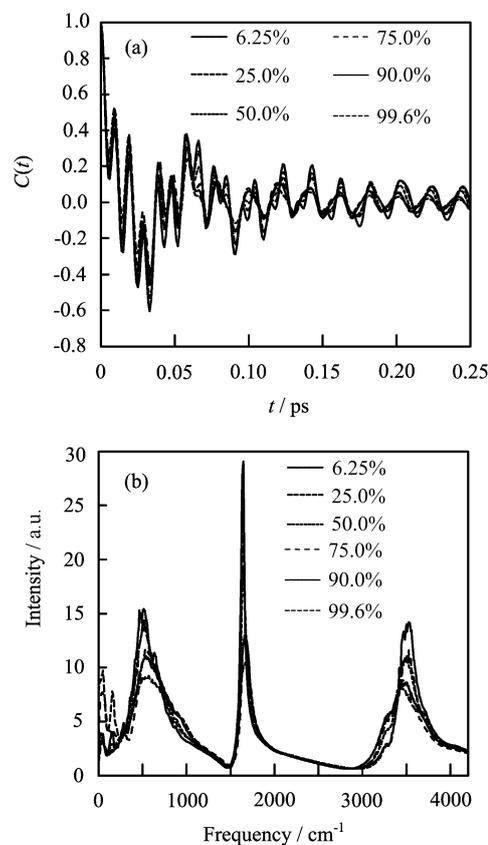


FIG. 2 The normalized hydrogen velocity time correlation function (a) and its power spectrum (b) of water molecules in the mixtures with different concentrations of water.

TABLE II The IR spectra of water in NaBF_4 /water mixture obtained by MD simulation.

$x_1/\%$	Frequencies/ cm^{-1}		
	Rotation	H-O-H bending	O-H stretch
6.25	487	1635	3530
25.0	513	1640	3505
50.0	528	1644	3484
75.0	554	1660	3462
90.0	567	1669	3452
99.6	575	1673	3443

tent with the far-IR measurements [46] and are corresponding to the hindered transitions [47]. The peak lies in $20-70 \text{ cm}^{-1}$ which is associated with the O-O-O flexing, the peaks lies in $120-180 \text{ cm}^{-1}$ and disappears for the high molar fraction of water which corresponds to water molecules that do not bond to each other via H-bonding. The peak lies $180-250 \text{ cm}^{-1}$ which is due to the hydrogen-bond O-H...O stretching of water dimers [40]. Our results agree well with the recent experimental results of water in ionic liquids contains BF_4^- [48]. In Ref.[48], it was concluded that a small contribution at 202 cm^{-1} can be attributed to intermolecular

interactions between water molecules forming dimmers, and the peaks centered at 148 cm^{-1} corresponds to water molecules that do not bond to each other via H-bonding.

Except that three peaks appearing below 250 cm^{-1} in Fig.2(b), there is significant increase in the magnitude of the spectral intensity at $250\text{--}750\text{ cm}^{-1}$ which comes from the rotation band of water, which agrees well with the experimental measurement in Ref.[48], at $1200\text{--}2000\text{ cm}^{-1}$ which derives from the bend band of water, and at $3200\text{--}4000\text{ cm}^{-1}$ due to the stretch vibration band of water. The rotational band 487 cm^{-1} of 6.25% water in $\text{NaBF}_4/\text{water}$ mixture are the same as the experimental value 459 cm^{-1} of 5% water in ionic liquids contains BF_4^- [48]. It is shown in Fig.2(b) and Table II that the rotation bands and the bending bands of water are red shift from 487 cm^{-1} to 575 cm^{-1} and from 1635 cm^{-1} to 1673 cm^{-1} respectively, whereas the O–H stretch bands are blue shift from 3530 cm^{-1} to 3443 cm^{-1} with the concentration of water in the mixture increase. It is an indication that the rotation and the H–O–H bending motion are hindered and the motion of rotation and bending become slower with in-

creasing the concentration of water, that is the hydrogen bond is formed easily with increasing the concentration of water. The same results can be obtained from the studies of the reorientation dynamics as follows. Our results agree well with the experiment result that when the rotation of the water molecules becomes hindered, the band moves to higher wavenumbers, the more hindered, the higher the wavenumber until the known rotational bands of liquid water [48].

C. Reorientation dynamics

To understand the reorientation dynamics of water molecules in $\text{NaBF}_4/\text{water}$ mixture, the rotational correlation functions $C_l(t)$ ($l=1,2$) for O–H vector and H–H vector of water molecule in $\text{NaBF}_4/\text{water}$ mixture are calculated from Eq.(3) during the simulations. The obtained results are shown in Fig.3 and Fig.4. One can see that the decay of $C_l(t)$ ($l=1,2$) in the mixture becomes slower as the molar fraction of water increases, the overall decay is not at all exponential, and the initial decay of rotational correlation functions are very fast on the time scale of 20 fs, followed by a pronounced beat

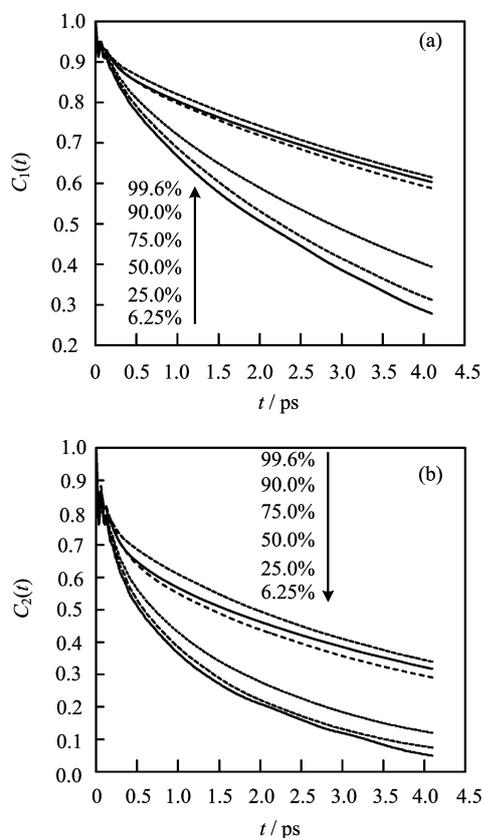


FIG. 3 Rotational correlation functions $C_1(t)$ (a) and $C_2(t)$ (b) of H_2O in $\text{NaBF}_4/\text{water}$ mixture with different concentrations of water, where \vec{u}^α is the O–H vector of water molecule.

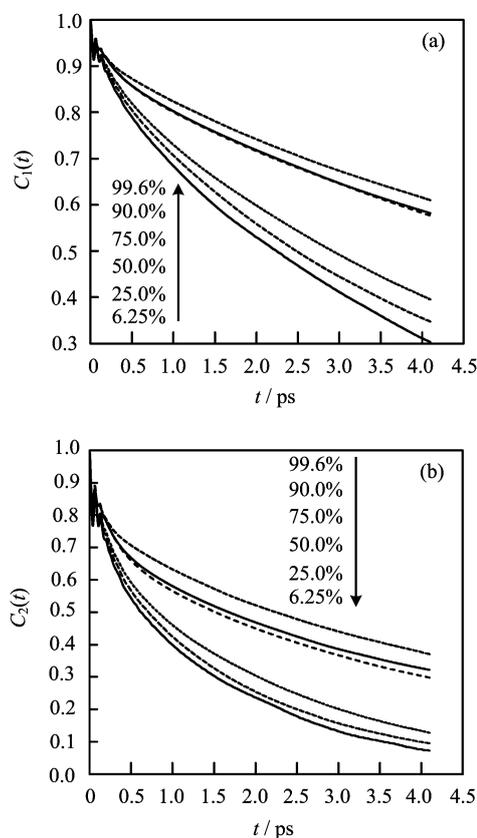


FIG. 4 Rotational correlation function $C_1(t)$ (a) and $C_2(t)$ (b) of H_2O in $\text{NaBF}_4/\text{water}$ mixture with different concentrations of water, where \vec{u}^α is the H–H vector of water molecule.

TABLE III The reorientation time (ps) of water in NaBF₄/water mixture.

$x_1/\%$	$\tau_1(\text{OH})$	$\tau_2(\text{OH})$	$\tau_1(\text{HH})$	$\tau_2(\text{HH})$
6.25	2.1752	1.1764	2.15958	1.17371
25.0	2.2713	1.23838	2.27800	1.26345
50.0	2.48542	1.33086	2.51555	1.42096
75.0	3.05622	2.00702	3.05958	2.06764
90.0	3.06235	2.10594	3.06333	2.17553
99.6	3.06335	2.10894	3.06633	2.21553

with a period of 80 fs, and a slower decay tail. According to our previous study [39], the initial fast decay and oscillation are due to the librations and hindered translations, where the librations and translations motions are hindered by the relative static structure of surrounding solvent molecules.

The rotation times calculated from Eq.(4) are given in Table III. To calculation the rotation time, a combined method has been used, using explicit integration until 0.5 ps, and fitted the tail of the correlation function after 0.5 ps to the exponent function, and obtained the integral for the tail from the fit. We also computed correlation times using a different time of division between explicit integral and fitting. All these give similar results, within 0.1 ps for the correlation time. Also, it is clearly shown that the rotational dynamics speeds down as the concentration of water in mixture is increased. With concentration of water in mixture increases, the hydrogen-bond interactions and the inharmonic interactions between the inter- or intro-molecular modes of water molecules are increased, therefore the molecules are hindered and the motions are difficult and more slow, which agree well with IR spectrum calculation in this work and the experiment observations [48].

IV. CONCLUSION

We have studied the structure, IR spectrum as well as rotational dynamics of water molecule in NaBF₄/water mixture at room temperatures with computer simulation. Various NaBF₄/water mixture with varying concentrations were used to understand the interactions and dynamics. In both liquids, water molecules tend to be isolated from each other in mixtures with more ions than water molecules. With the increase of the concentration of water in the mixture, the rotation bands and the bending bands of water display red shift from 487 cm⁻¹ to 575 cm⁻¹ and from 1635 cm⁻¹ to 1673 cm⁻¹ respectively, whereas the O–H stretch bands show blue shift from 3530 cm⁻¹ to 3443 cm⁻¹, and the decay of the reorientation correlation function becomes slower. This suggests that the molecules are hindered and their motions are difficult and slow with the increase of the concentration of water in mixture, due to

the hydrogen-bond interactions and the inharmonic interactions between the inter- or intra-molecular modes which agree well with the experiment results. Our results of the O–H stretch band of water in NaBF₄/water mixture make predictions for the experimental verifications.

V. ACKNOWLEDGMENTS

The authors are grateful to Professor Jiu-shu Shao at Beijing Normal University for his encourage and help reading the manuscript. We also would like to thank Prof. Jian-min Tao and Guo-bao Li for their kind help. This work was supported by the National Natural Science Foundation of China (No.50564006), the Key program of Natural Science Foundation of Yunnan Province (No.2005E0004Z), the Natural Science Foundation of Yunnan Province (No.2008E0049M), the Foundation of the Education Department of Yunnan Province (No.07Z40082), and the Foundation of Kunming University of Science and Technology (No.2007-16).

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