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RESEARCH ARTICLE

Seeing Molecules in Motion in Aqueous Solutions

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Abstract Hydrogen bonds play critical roles in determining the structural, thermodynamic and dynamical behavior of water and aqueous solutions. In solutions of ions in water, the hydrogen bonded network can be perturbed significantly by the presence of ions. This perturbation, in turn, changes many of the equilibrium and dynamical properties of water in the solutions compared to those in pure water. The network of hydrogen bonds is dynamic in nature. It fluctuates at a very fast rate due to breaking and reformation of hydrogen bonds. In the present article, a brief review is made of some of the recent computer simulation studies to 'see' these hydrogen bonded molecules in motion in aqueous solutions. Connections of the simulation results are also made to some of the recent experimental studies on aqueous solutions using the method of time dependent infrared spectroscopy.

Keywords Molecular simulations · Dynamics of liquids · Aqueous solutions

1 Introduction

ichard Feynman famously said in his 1963 *Lectures on Physics* "Everything that living things do can be understood in terms of the jiggling and wiggling of atoms". The Rahman 1964 paper on "Correlations in the Motion of Atoms in Liquid Argon" [1] opened the era of molecular dynamics simulations to see these 'jiggling and wiggling' of atoms in liquids in virtual laboratories set up in computers. Water is 'The Liquid' of nature. The structure and dynamics of water are primarily determined by the strong and directional intermolecular hydrogen bonds between oxygen and hydrogen atoms. In an ideal scenario, each water molecule would have four hydrogen bonds but in reality it is less by about 10–12 % in the liquid phase due to thermal fluctuations [2]. In liquid water, hydrogen bonds break and reform at an amazingly fast rate due to the cooperative nature of such phenomena. The dynamics of hydrogen bond fluctuations influence just about every chemical process in water in one way or the other [3]. When ions are dissolved, the structure of water is perturbed. Presence of ions affects the local density and orientation of water molecules and can even lead to formation of new hydrogen bonds of different characters. Hence, the structure and dynamics of aqueous ionic solutions can be rather different from those of pure water. A molecular understanding of such changes requires an in-depth study of the perturbation of hydrogen bonds by ions both structurally and dynamically.

There have been many experimental studies based on infrared and Raman spectroscopic measurements [4–6], extended X-ray absorption fine structural spectroscopy [7, 8], neutron diffraction with isotopic substitution [9–11], nonlinear time dependent infrared spectroscopy over the years to elucidate the effects of ions on hydrogen bonding network in water. The most successful among them have been the recent time dependent infrared spectroscopic studies [12–15] which have provided a rather detailed picture of the dynamical nature of hydrogen bonded network in water and how is the network perturbed by the presence of ions. In spite of all these experimental studies, computer simulations still perhaps offer the most important tool to investigate the structural and dynamic properties of aqueous ionic solutions at molecular level.

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Recent experiments using femtosecond pump probe spectroscopy showed that the rotational dynamics of water molecules are not significantly affected by ions beyond their first solvation shells, even for concentrations as high as 6 M. This led to the conclusion that the hydrogen boned network essentially remains unchanged beyond the first solvation shell. The hydrogen bond dynamics of solvation shells of halide ions in water were initially reported to be an order of magnitude slower [12, 13]. These studies of hydrogen bond dynamics were based on time dependent investigations of the so-called vibrational spectral diffusion arising from vibrational frequency fluctuations due to fluctuations in hydrogen bonds. However, more recent infrared transient absorption and two-dimensional infrared studies [14, 15] reported that the spectral diffusion and hydrogen bond dynamics of water in the solvation shells of halide ions could be slower by a factor of 2–4 compared to that in bulk water at room temperature. Also, the dynamics was found to become slower with increase of ion concentration.

On the theoretical side, the structure and dynamics of aqueous ionic solutions have been studied through many computer simulation studies using a variety of simulation methods. The dynamics of hydrogen bond fluctuations and vibrational spectral diffusion have been investigated first through classical molecular dynamics [16–18] and then by means of ab initio molecular dynamics [19–21]. In the present article, we make a brief review of some of the recent theoretical work in this area. Clearly, we do not intend to be exhaustive. In the next Section, we give a brief account of the methodologies used in theoretical calculations and in Sect. 3, we describe some of the results on both the structural and dynamical aspects of hydrogen bonds. Our conclusions are briefly summarized in Sect. 4.

2 Simulation Methods for Calculations of Dynamical Network of Hydrogen Bonds

Both classical and ab initio molecular dynamics simulations have been performed to investigate the dynamical network of hydrogen bonds in water and aqueous ionic solutions [16–21]. In classical molecular dynamics simulations, one uses pre-defined empirical interaction potentials to model various inter-molecular interactions. For water, most of the recent studies have employed the so-called three-site SPC/E [22] or similar multi-site models whereas for ions, one typically uses the models of Lennard-Jones particles with charges [23–25]. The parameters of these models are well-tuned to provide good description of water and aqueous solutions at room temperature. Specifically, we will be discussing about aqueous solutions of sodium chloride and sodium bromide solutions for which the details of various parameters are available in above-mentioned references.

We note that essentially all of the available empirical potentials of water and ions are developed for ambient water. They are not readily applicable to non-ambient thermodynamic conditions. Also, changes of electronic structure of the solvent with varying ion concentration are generally not incorporated in the empirical models. The method of ab initio molecular dynamics goes beyond the use of such pre-defined empirical potentials and incorporates a full quantum mechanical description of the inter-particle interactions. Specifically, the Car–Parrinello and Born–Oppenheimer molecular dynamics methods have made possible simulations of liquid water purely from first principles [26, 27]. These simulation methods consider electronic degrees of freedom through quantum density functional theory (DFT) and the ionic motion by classical dynamics at a finite temperature. Quantum mechanical methods other than DFT for electronic structure calculations have also been used. Since no predefined empirical potentials are used in these methods, they are ideally suited for studying complex liquids such as water under a variety of thermodynamic conditions and chemical environments. It may be noted that the ab initio molecular dynamics simulations are computationally much more expensive than classical simulations which use empirical interaction potentials. However, recent increase in high performance computing power coupled with more efficient algorithms have made ab initio simulation a powerful method in practice for investigating various complex chemical processes at different thermodynamic conditions.

3 Hydrogen Bonds and Vibrational Spectral Diffusion

Generally in liquid state theories of hydrogen bonded liquids, a set of geometric criteria is used to define a hydrogen bond. However, other kinds of definitions, say based on energetic criteria, are also available in the literature. In the following, we discuss some of the results of hydrogen bonds in aqueous solutions using geometric criteria as described in Ref. [16–21]. Two water molecules are said to be hydrogen bonded if their inter-oxygen distance is <3.5 Å and simultaneously hydrogen–oxygen distance is <2.45 Å. A chloride ion is said to be hydrogen bonded with a water molecule if the chloride-oxygen distance is <3.90 Å and simultaneously the hydrogen-chloride distance is <3.05 Å. Similarly, hydrogen bonds with other solute ions can also be defined using proper cut-off distances for ion-oxygen and ion-hydrogen distances. We note that these cutoff distances are determined from the relevant pair correlation functions of the ion-water systems. We also note that, in addition to distance cut-offs, sometimes angle cut-offs are also used in the definition of hydrogen bonds.

The numbers in Table 1 shows how the hydrogen bonded structure is affected by the presence of ions. It can be seen that the number of water–water hydrogen bonds decreases significantly in the vicinity of ions. The change is more significant at higher ion concentration. However, a good part of the loss of water–water hydrogen bonds is compensated by the formation of new ion-water hydrogen bonds, so that the net number of hydrogen bonds per water does not change much beyond the first solvation shell. These results can be corroborated with earlier spectroscopic findings of aqueous ionic solutions [12, 13]. The results discussed above are for classical molecular dynamics of aqueous NaCl solutions [18]. Ab initio molecular dynamics simulations have also been carried out for a variety of aqueous ionic solutions to explore the perturbation of hydrogen bonds by ions [19–21]. These simulations have also revealed that the number of water–water hydrogen bonds is reduced significantly in the vicinity of halide ions, however some the lost water–water hydrogen bonds are compensated by newly formed anion-water hydrogen bonds. In particular, each of the chloride and bromide ions were found to form about five hydrogen bonds with surrounding water molecules [19–21].

Apart from the hydrogen bonded structure, the dynamics of hydrogen bonds has also been investigated for many aqueous ionic solutions by means of both classical molecular dynamics and ab initio molecular dynamics simulations [16–21]. These studies have generally shown a slowing down of the dynamics with ion concentration for diffusion and orientational relaxation. The dynamics of hydrogen bonds are directly looked at by constructing suitable time correlation functions of hydrogen bond population variables. The underlying dynamics can also be investigated indirectly through calculations of frequency time correlations of stretch modes of water. The frequencies of stretch modes of water are greatly dependent on the nature of the associated hydrogen bonds, hence any fluctuation in the associated hydrogen bond would alter the stretch frequency. Thus, the fluctuation dynamics of the stretch frequencies would capture the dynamics of hydrogen bonds. It may be noted that this correlation forms the basis of the interpretation of all time dependent infrared spectroscopic results of vibrational spectral diffusion.

In the following, we discuss some of the results of aqueous ionic solutions at quantitative level. These results are from ab initio molecular dynamics of aqueous NaCl, NaBr and NaI solutions. For NaCl solution, the dynamics of frequency fluctuations, or the vibrational spectral dynamics, was found to occur in time scale of about 2 ps at low concentration having only one Cl$^-$ ion and it slows down to about 3 ps when the concentration is increased to about 3.5 M. For NaI solutions, the relevant time scales of spectral diffusion are 2.2 ps for only one ion in water and 3.3 ps for a concentrated solution. These results are in general agreement with time dependent infrared spectroscopic results of Ref. [14]. Thus, the simulations were found to correctly predict how the dynamics of vibrational spectral diffusion slows down with ion concentration. Regarding the hydrogen bond dynamics, it was, however, found that the bromide-water and iodide-water hydrogen bonds are weaker than water–water hydrogen bonds and, in fact, these ion-water hydrogen bonds have shorter lifetimes than water–water hydrogen bonds. Since the number of ion-water hydrogen bonds increases with ion concentration, the dynamics of overall hydrogen bonds would become faster with increase of ion concentration. Still, the spectral diffusion was found to slow down. This meant that apart from hydrogen bond fluctuations, other dynamics modes such as rotation are also involved in influencing the dynamics of spectral diffusion. A more quantitative analysis of this aspect is available in Ref. [20, 21].

4 Conclusions

In this article, we have presented a brief review of some of the recent studies aimed at investigating the motion of molecules in aqueous solutions. We have described the power of molecular dynamics simulations in unraveling the ‘jiggling and wiggling’ of atoms in the solutions. The roles of recent time dependent infrared spectroscopy as a powerful experimental tool for such studies are also discussed. Specifically, we have discussed some of the recent results of the structure and dynamics of hydrogen bond network in

Table 1 The average number of hydrogen bonds per water molecule N_{HB} in infinitely dilute and 5.3 M NaCl solutions at 298 K [18]

	Cl$^-$ first shell	Cl$^-$ second shell	Na$^+$ first shell	Na$^+$ second shell	Bulk water
Water–water	2.86	3.78	2.53	3.82	3.75
Infinitely dilute 5.3 M	2.10	2.76	1.96	2.79	2.68
Water–water and ion water	3.81	3.78	2.53	3.82	3.76
Infinitely dilute 5.3 M	3.22	3.25	2.53	3.47	3.29

aqueous solutions. We have discussed how the structure and dynamics of the hydrogen bonds get affected by the presence of ions. We have analyzed the average number of hydrogen bonds per water molecule, first considering only water–water hydrogen bonds and then considering both water–water as well as ion-water hydrogen bonds. It is reported that although the number of water–water hydrogen bonds is significantly reduced in the first solvation shell of the ions, a good part of the loss is compensated by the formation of ion-water hydrogen bonds. With increase in concentration, the ion-water hydrogen bonds are found to replace many of the water–water hydrogen bonds.

On the dynamical side, results are discussed for the effects of ions on the dynamics of hydrogen bond fluctuations and vibrational spectral diffusion. The vibrational spectral diffusion of the stretch modes of water arises from frequency fluctuations due to fluctuations in the associated hydrogen bonds. Generally, it is found that the presence of ions slow down the dynamics of vibrational spectral diffusion which is in agreement with recent time dependent infrared spectroscopic experiments. The dynamics of hydrogen bonds, however, can be both slower [19] or faster [20, 21] depending on the nature of ions. For bromide and iodide ions, the ion-water hydrogen bonds relax at a faster rate than water–water hydrogen bonds as the former are weaker hydrogen bonds. These results imply that other modes of motion also influence the dynamical characteristics of vibrational spectral diffusion. For example, rotational motion of water in the vicinity of ions or the reformation dynamics of water from a non-hydrogen bonded state to a hydrogen bonded state can also alter the frequency of the concerned stretch modes of water, hence can influence the dynamics of vibrational spectral diffusion in aqueous ionic solutions.

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