The relation between the structure of the first solvation shell and the IR spectra of aqueous solutions

Revati Kumar · Tom Keyes

Received: 14 June 2011 / Accepted: 4 October 2011 /
Published online: 3 November 2011
© Springer Science+Business Media B.V. 2011

Abstract The spectroscopic signatures of solvated anions and cations, in the O-H stretch region of water, are studied using the POLIR potential. Shifts in the spectra are shown to correlate very well with the distribution of a particular hydrogen bond angle for the waters in the first solvation shell. The results indicate that the spectral shifts might be predicted from MD simulations in a computationally convenient fashion, avoiding an explicit calculation of the spectra, as first suggested by Sharp et al. (J Chem Phys 114(4):1791–1796, 2001).

Keywords Ions · Solvation shell · Hydrogen bond angles · IR spectra

1 Introduction

The anomalous properties of water, such as the relatively high and low density of its liquid and solid states, the high specific heat capacity of the liquid, the high melting point, etc., have a profound impact on the behavior of both biological and chemical systems [2]. It is generally believed that the distinctive behavior of water arises from the underlying hydrogen bond network [3, 4]. While the nature of aqueous hydrogen bonds has been under considerable debate in the literature, their spectroscopic signatures have been well documented [5–7]. The red shift of the O-H stretch upon condensation is a prime example.

In biology, water does not exist as a neat liquid but rather as a solution with a number of solutes, charged and uncharged, which affect the hydrogen bond network, and thence the IR spectrum [8, 9]. (Biological water is also interacting with macromolecules and complex nanostructures, but solvation is the focus of this article.) For example, magnesium ions cause a red shift in the O-H region of the spectrum of the solvating waters [10]. Chloride ions, on the other hand, cause a blue shift [10]. Madan and Sharp have investigated how

R. Kumar · T. Keyes (✉)
Department of Chemistry, Boston University, Boston, MA 02215, USA
e-mail: keyes@bu.edu

solutes perturb the hydrogen bond network [11–13], and Sharp, Madan, and Vanderkooi have further attempted to correlate the spectroscopic shifts to these changes [1]. They considered a few alkali halide solutes and an uncharged hydrophobic solute, TMAO, and demonstrated that the former showed a greater fraction of distorted hydrogen bonds compared to neat water, while the latter had a larger number of undistorted hydrogen bonds [1].

The POLIR polarizable water potential was developed in our group with the specific aim of describing vibrational spectra [14]. After being first tested on liquid water, clusters, and ice, POLIR was recently applied to aqueous solutions of the divalent metal cations magnesium, calcium, and copper [15]. It successfully reproduced the experimental IR shifts reported in the literature.

In this paper, we attempt to understand how spectral shifts depend upon ion charge and hydrophobicity. To this end, we consider an anion, chloride, for the first time. The chloride–water interaction is determined using results from *ab initio* calculations on the water–chloride dimer, as in our prior calculations on the magnesium ion. For a broad range of solutes, we also considered Mg^{2+} and hypothetical cations formed by setting the charge on the chloride ion to +0.1, giving rise to a very weakly hydrophobic solute, and by setting the charge on magnesium to 0 and +1, keeping all other parameters the same as on the “real” ions. We then extended the treatment of Madan et al. to include these solutes, thus forming a more complete understanding of the correlation between their effect on the hydrogen bond network and the spectroscopic shifts.

The paper is organized as follows. Section 2 addresses the development of the ion–water potential as well as the methods used to determine the IR spectra of the first solvation shell and the definition of the hydrogen bond. The results are discussed in Section 3 and our conclusions are presented in Section 5.

2 Methodology and computational details

POLIR is a three-site model, described in detail in [14], with atomic charges, permanent dipoles, polarizabilities, and the corresponding induced dipoles, and a van der Waals pair interaction expressed in terms of the O–O distance. The electrostatic interactions are damped following Thole [16].

POLIR has previously been used to study the solvation of the divalent cations magnesium, calcium, and copper, and the polarizable ion–water potentials have been determined [15]. Here we present our approach to deriving solute–water potentials consistent with POLIR, with application to Cl^- . The Mg^{2+} –water potential is taken from the previous study.

2.1 Development of the ion–water potential

The chloride ion is represented as a point charge of $-1e$ and is assigned a polarizability of 4 Å, which was taken from the literature [17]. The van der Waals interaction is expressed as a function of the distance between the ion and the O atom of the water with the functional form

$$U_{vdW} = \frac{A_{16}}{r_{iO}^{16}} + \frac{A_{14}}{r_{iO}^{14}} + \frac{A_{12}}{r_{iO}^{12}} + \frac{A_6}{r_{iO}^6} \quad (1)$$

We fit the Thole damping constants for the charge-dipole (a_{CD}) and dipole-dipole (a_{DD}) interactions, and the van der Waals constants, to reproduce the *ab initio* potential energy scan, using the aug-cc-pVTZ basis set at the MP2 level of theory, of the ion-water dimer (Fig. 1).

Once the potential was determined, we performed five sets of MD simulations in the NVE ensemble at an average temperature of 300 K and with a cubic simulation box of length 15.64 Å. In each case, the box contained one solute and 127 water molecules. The five simulations corresponded to the use of the following five solutes:

1. Cl^-
2. Chloride with the charge changed to +0.1, but otherwise as in 1.
3. Mg^{2+}
4. Magnesium with the charge set to +1, but otherwise as in 3.
5. Magnesium with the charge set to 0, but otherwise as in 3.

2.2 IR spectroscopy

In the classical approach, the IR spectrum is obtained as follows [18]

$$I(\omega) = \frac{4\pi^2\omega}{3cV\hbar}(1 - e^{-\beta\hbar\omega}) \cdot Q(\omega) \cdot C(\omega), \quad (2)$$

where $C(\omega)$ is the Fourier transform of the total simulation box dipole moment time autocorrelation function, $C(t)$, including permanent dipoles and induced dipoles.

Our argument is not that quantum mechanics is unnecessary, but that only simple quantum corrections to the classical $C(\omega)$ are required. These are the harmonic intensity correction, $Q(\omega)$, and an anharmonic frequency correction [19], amounting to a red shift of 184 cm^{-1} for the O-H stretch of water. This anharmonicity correction has been discussed in detail in previous papers; our finding that it is quite constant over diverse environments is crucial to this work [14, 15].

Here we present “first shell” spectra calculated from the autocorrelation function of the total dipole in the first solvation shell around each solute, defined using the first minimum in the solute-O radial distribution function as the cutoff r_c . It should be noted that the induced dipoles of the first shell waters have been determined using the total electric field of the box, and that the total spectrum will contain cross-correlations between the first-shell dipole and the remaining dipole. Nevertheless, these spectra provide the clearest picture of the effect of the solutes.

Fig. 1 The optimized Cl^- ion-water dimer

Fig. 2 Two definitions of the hydrogen bond angles, β and α . Note that there are four possible O–O–H angles and β is the smallest of the four

2.3 Hydrogen bond angle

The hydrogen bond angle used in our analysis is based on the work of Madan and Sharp [1, 11–13]. They defined two water molecules to be hydrogen bonded if the O–O distance was less than 3.4 Å. Then, the hydrogen bond angle, β , was given by the smallest of the four possible O–O–H angles (see Fig. 2).

3 Results

The ab initio potential energy scan (PES) for the chloride ion-water dimer is shown in Fig. 3. It is clear that our model, with electrostatic and van der Waals terms, does a good job in reproducing the PES. The parameters are given in Table 1.

Fig. 3 The potential energy scan of the Cl^- ion-water dimer

Table 1 Parameters for the Cl^- -water interaction

Parameter	Value
A_{16} (kcal/mol)/ $\text{\AA}^{16}$	108.871×10^5
A_{14} (kcal/mol)/ $\text{\AA}^{14}$	-94.2448×10^5
A_{12} (kcal/mol)/ $\text{\AA}^{12}$	21.042×10^5
A_6 (kcal/mol)/ $\text{\AA}^6$	$-2,082.49$
The Thole damping constants for the charge-charge, charge-dipole and dipole-dipole interactions are denoted a_{CC} , a_{CD} , and a_{DD} , respectively	
a_{CD}	0.1
a_{DD}	0.3
a_{CC}	0.5
$\alpha_{CI}/\text{\AA}^3$	4.0

3.1 Structure of the solvation shell

Figure 4 shows the solute-O radial distribution functions for the five different cases discussed earlier. The first minimum defines the cut-off for the first solvation shell. The distribution of intra-shell hydrogen bond angles, β , for each of the five solutes, along with the distribution for neat water, is plotted in Fig. 5. Previously, we discussed a distribution of β , which included hydrogen bonds made by first-shell waters to second-shell waters [15]. Here, by including intra-first-shell hydrogen bonds only, we obtain an even more sensitive indicator of the IR spectrum.

Neat water shows two peaks in the distribution of β . Madan and Sharp assign the peak at small angles and the peak at around 52° to undistorted and distorted hydrogen bonds, respectively. Their idea is that the effect of solutes on the IR spectra may be understood through the changes they induce in the populations of the two types of hydrogen bonds, i.e., in the relative areas of the two peaks.

In the case of Cl^- , the fraction of distorted hydrogen bonds increases compared to neat water. Magnesium with a charge of 0 shows a smaller increase. The chloride solute with a charge of +0.1 has fewer distorted bonds than does neat water.

Mg^{2+} presents new and different behavior. The water molecules in the first solvation shell show extremely distorted hydrogen bond angles, which are not seen in neat water at all. The distribution is peaked at around 85° , and the characteristic peaks seen in neat water, and with the solutes just discussed, are absent. Magnesium with charge +1 shows both

Fig. 4 The solute-O radial distribution function for the various solutes

Fig. 5 The distribution of the hydrogen bond angle, β , of water molecules in the first solvation shell. For a hydrogen bond, the O–O distance between two water molecules, both of which are in the first shell, must be less than 3.4 Å

distorted and extremely distorted hydrogen bonds, and is intermediate between the Mg^{2+} case and the other solutes.

3.2 IR spectra of the first solvation shell

The first-shell IR spectra, specifically the O–H stretch region, are shown in Fig. 6. Cl^- shows a clear blue shift from the neat water spectrum, in agreement with experiment [1], and Mg^{2+} shows a red shift, also in agreement [10]. Magnesium with 0 charge shows a slight blue shift while the chloride with charge of +0.1 shows a slight red shift with respect to neat water. Magnesium with a charge of +1 shows a broad spectrum with two peaks, one of which is slightly red shifted while the other is slightly blue shifted.

For Cl^- and Mg^{2+} , a more direct comparison with experiment would obviously be desirable, but we cannot do it at this point for two reasons: 1. The experiments observe the OD stretch in $\text{HOD}/\text{H}_2\text{O}$ mixtures, while we simulate H_2O , and 2. Experiments must include an anion as well as a cation, with the contribution of an individual ion not directly

Fig. 6 The IR spectra in the O–H stretch region of the first solvation shell around each solute

available, but deduced from some data analysis. Thus we must be satisfied with reproducing the qualitative trends, and will consider ion pairs in future work.

4 Discussion

Madan, Sharp et al. have related the shifts in the solution spectra to the nature of hydrogen bonds in the first solvation shell, within the framework of the two-state picture suggested by the two peaks in the distribution of β discussed above. The solutes are observed to modify the relative amplitudes of the peaks for “undistorted” and “distorted” hydrogen bonds already present in neat water. Strong, undistorted hydrogen bonds decrease the OH stretching frequency, so, compared to neat water, less distortion causes a red shift, and vice versa.

Using MD simulations with simple pairwise potentials, Madan, Sharp and colleagues correlated the effect of solutes like KCl and TMAO on the hydrogen bond angle distribution to the shifts in the experimentally observed IR spectra. They verified that TMAO and KCl, with red and blue shifts, indeed had smaller and larger percentages of distorted hydrogen bonds than neat water, respectively. Furthermore, they connected the angle distribution to the nature of the solute, arguing that hydrophilic solutes, with a strong solute-water interaction, directly distorted the network, while hydrophobic solutes replaced waters that already had distorted bonds, resulting in less distortion.

We confirm the basic ideas of Madan et al. However, their picture neglected ions with large charge-to-radius ratios like Mg^{2+} . Furthermore, they did not have a water potential like POLIR capable of producing the spectra, as well as the first-shell β distributions, from the same simulation. Here we attempt a more complete treatment of the effect of the hydrogen bond arrangements in the first solvation shell on the IR spectrum. It begins by introducing a β -distribution particularly sensitive to the solute, namely, the intra-first-shell distribution.

Our three more weakly interacting solutes, Cl^{-1} , Mg^0 , and $\text{Cl}^{+0.1}$, follow the two-state picture. The magnitude of the first peak in $g(r)$ clearly shows (Fig. 4) that Cl^{-} is hydrophilic, Mg^0 is slightly hydrophilic, and $\text{Cl}^{+0.1}$ is hydrophobic. Note that Mg^0 is not a real solute, and is made hydrophilic by the strong van der Waals attraction belonging to Mg^{2+} . Also, in the case of Cl, the first minimum in the solute-O radial distribution functions is much farther away compared to the Mg-based solutes, indicating the much larger size of the solvation shell.

The β -distributions (Fig. 5) are in perfect accord, with the “distorted” peak of Cl^{-1} much higher than in neat water, that of Mg^0 slightly higher, and with $\text{Cl}^{+0.1}$ having fewer distorted hydrogen bonds than neat water. Moreover, the spectra behave as expected, with the waters around the Cl^{-} exhibiting a net blue shift compared to neat water, and Mg^0 having a small blue shift. Our hydrophobic solute, $\text{Cl}^{+0.1}$, has a slight red shift. This case is similar to the TMAO solute discussed by Sharp et al. [1].

TMAO was observed to have hydrophobic and hydrophilic regions [1]. Our aim in combining a weakly hydrophobic van der Waals potential with a weakly hydrophilic Coulomb interaction in $\text{Cl}^{+0.1}$ was to obtain something representative of TMAO, given the limitations of using a single ion.

With Mg^{2+} , a new feature appears, namely, a large-angle peak corresponding to “extremely distorted” hydrogen bonds which do not appear at all in pure water. This peak is the

signature of an extremely strong solute–solvent interaction, from a large charge-to-radius ratio. Actually, hydrogen bonds with such large angles are not physically meaningful bonds. Furthermore, β shows negligible values at both the first and second maximum exhibited by liquid water. For Mg^{2+} , there is no “normal” hydrogen bonding in the first shell.

Why, then, does Mg^{2+} show the large red shift seen in Fig. 6? Very simply, the strong solute–water interaction directly weakens the force constant of the covalent O–H bond; there are more influences on the frequency than hydrogen bonding. Fortunately, the strong interaction has a negligible effect on the quantum anharmonic frequency correction, so the resulting shifts in the spectrum are accurately captured by the classical dipole correlation.

One might ask if the distinctive behavior of Mg^{2+} follows from the charge alone. An answer can be found in our prior study [15] of Ca^{2+} , which is larger than Mg^{2+} , with the first peak in the water-ion $g(r)$ at $\approx 2.43 \text{ \AA}$ vs $\approx 2.05 \text{ \AA}$. Ca^{2+} shows a small blue shift and no large-angle peak in the hydrogen bond angle, β , so we must conclude that small size is essential to forming the strongest interactions.

When the charge is lowered to $+1$, keeping all the parameters the same, the interactions weakens. The solute–O radial distribution function is slightly pushed out with respect to Mg^{2+} , and the peak in the distribution of the first-shell hydrogen bond angles, β , is shifted to lower values. Some “distorted” angles from neat water are now visible, although the shell is still too tightly held to see undistorted angles. Accordingly (Fig. 6), the spectrum of Mg^{1+} is slightly red shifted.

5 Conclusions

In this paper, we have demonstrated a clear link between the hydrogen bond angle distribution in the first solvation shell, and the spectroscopic features in the IR spectrum of a solution. The intra-first-shell distribution is an even better indicator than the distribution including hydrogen bonds to the second shell. We present a clear progression from red shifts to blue shifts with respect to neat water as we change the solute.

As was first explained by Sharp and Madan, for weak to moderate solute–water interaction strengths, the distribution of angles in the first shell resembles that of neat water, but with changes in the amplitudes of the two peaks. Then, a smaller or larger fraction of distorted bonds indicates a red or blue shift, respectively. For the strongest interactions, a third peak appears, absent in neat water, indicating that there are no meaningful hydrogen bonds in the first shell, and the spectrum will be redshifted by direct interaction of the solute with the covalent OH bond.

In short, our work suggests that the spectroscopic features of a solution may be predicted by simply observing the hydrogen bond angle distribution in the first shell, and that the distribution may be anticipated based on hydrophobicity.

Acknowledgements We thank the donors of the American Chemical Society Petroleum Research Fund and the National Science Foundation (grant CHE 0848427) for support of this research.

References

1. Sharp, K.A., Madan, B., Manas, E., Vanderkooi, J.M.: Water structure changes induced by hydrophobic and polar solutes revealed by simulations and infrared spectroscopy. *J. Chem. Phys.* **114**(4), 1791–1796 (2001)

2. Franks, F.E.: Water: a Comprehensive Treatise. Plenum, New York (1972)
3. Stillinger, F.H.: Water revisited. *Science* **209**(4455), 451–457 (1980)
4. Kumar, R., Schmidt, J.R., Skinner, J.L.: Hydrogen bonding definitions and dynamics in liquid water. *J. Chem. Phys.* **126**(20), 204107 (2007)
5. Senior, W.A., Verrall, R.E.: Spectroscopic evidence for the mixture model in HOD solutions. *J. Phys. Chem.* **73**(12), 4242–4249 (1969)
6. Hare, D.E., Sorensen, C.M.: Raman spectroscopic study of dilute HOD in liquid H₂O in the temperature range – 31.5 to 160°C. *J. Chem. Phys.* **93**(10), 6954–6961 (1990)
7. Fecko, C.J., Loparo, J.J., Roberts, S.T., Tokmakoff, A.: Local hydrogen bonding dynamics and collective reorganization in water: ultrafast infrared spectroscopy of HOD/D₂O. *J. Chem. Phys.* **122**(5), 054506 (2005)
8. Lin, Y.-S., Auer, B.M., Skinner, J.L.: Water structure, dynamics, and vibrational spectroscopy in sodium bromide solutions. *J. Chem. Phys.* **131**(14), 144511 (2009)
9. Bakker, H.J., Skinner, J.L.: Vibrational spectroscopy as a probe of structure and dynamics in liquid water. *Chem. Rev.* **110**(3), 1498–1517 (2010)
10. Stangret, J., Gampe, T.: Ionic hydration behavior derived from infrared spectra in HDO. *J. Phys. Chem. A* **106**(21), 5393–5402 (2002)
11. Madan, B., Sharp, K.: Heat capacity changes accompanying hydrophobic and ionic solvation: A Monte Carlo and random network model study. *J. Phys. Chem.* **100**, 7713–7721 (1996)
12. Sharp, K., Madan, B.: Hydrophobic effect, water structure, and heat capacity changes. *J. Phys. Chem. B* **101**(18), 4343–4348 (1997)
13. Madan, B., Sharp, K.: Changes in water structure induced by a hydrophobic solute probed by simulation of the water hydrogen bond angle and radial distribution functions. *Biophys. Chem.* **78**(1–2), 33 (1999)
14. Mankoo, P.K., Keyes, T.: POLIR: polarizable, flexible, transferable water potential optimized for IR spectroscopy. *J. Chem. Phys.* **129**(3) 034504-1–034504-9 (2008)
15. Kumar, R., Keyes, T.: Classical simulations with the POLIR potential describe the vibrational spectroscopy and energetics of hydration: divalent cations, from solvation to coordination complex. *J. Am. Chem. Soc.* **133**, 9441 (2011)
16. Thole, B.T.: Molecular polarizabilities calculated with a modified dipole interaction. *Chem. Phys.* **59**(3), 341–350 (1981)
17. Grossfield, A., Ren, P., Ponder, J.W.: Ion solvation thermodynamics from simulation with a polarizable force field. *J. Am. Chem. Soc.* **125**(50), 15671–15682 (2003)
18. Ahlborn, H., Space, B., Moore, P.B.: The effect of isotopic substitution and detailed balance on the infrared spectroscopy of water: a combined time correlation function and instantaneous normal mode analysis. *J. Chem. Phys.* **112**(18), 8083–8088 (2000)
19. Berens, P., Wilson, K.R.: Molecular dynamics and spectra. I. *J. Chem. Phys.* **74**, 4872 (1981)