

Ratiometric detection of Raman hydration shell spectra

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The micro-structure of hydration shell of solute in water is significant for understanding the properties of aqueous solutions. However the spectra of hydration shell are difficult to be obtained. Herein, a novel Raman ratio spectra, which is obtained through dividing the Raman spectra of aqueous solutions from the spectrum of water, was applied to deduce the spectra of hydration shell of organic (acetone-D6) and inorganic compounds (NaNO₃, NaSCN, NaClO₄, Na₂SO₄, NaCl) in water. Those spectra of the hydration shell were employed to study the micro-structures of the first hydration shells of anions, the number of water molecules in the first hydration shell of free anions and acetone-D6, and the aggregation behavior of ions in the concentrated aqueous NaNO₃. The number of water molecules in the hydration shell was supported by our molecular dynamic simulations. The Raman ratio spectra can be widely employed to obtain the spectra of the first hydration shell, and it is helpful to understand the micro-structure of aqueous solutions. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: Raman spectroscopy; ratio spectra; hydration shell; hydration number; micro-structure

Introduction

Aqueous solutions widely exist in seawater, human body, electrolyte, and so on. The properties of solutions are dependent on the micro-structure of solutions.^[1–6] The structure is usually studied in the dynamic and statistical viewpoint. The dynamic structure has been researched through femtosecond 2D IR spectroscopy, ultrafast pump-probe spectroscopy^[7–16] and MD simulations.^[17–19] Using these methods, the information of vibrational or rotational relaxation dynamics of water molecules in hydration shell is acquired. On the other hand, the statistical structure has been widely studied through MD simulations,^[17,19–22] Raman and IR spectroscopy^[23–28], X-ray and neutron diffraction.^[29–33] Employing these methods, the hydrogen bond length and angles, the hydration number, and the spatial distribution of water molecules in hydration-shell are obtained. Whether in the dynamic viewpoint or statistical viewpoint, the central issue about the microstructure of aqueous solutions is the hydration shell of solute.

Hydration shell has been widely studied through vibrational spectra in OH stretching region. This is because the intermolecular interactions between solutes and water molecules strongly affect the OH stretching vibration. The vibrational spectra of water in hydration shell are different from the spectra in bulk water; however, they overlap seriously with each other and can hardly be distinguished. Recently, plenty of methods were employed to extract the spectra of hydration shell from the overlapping spectra, such as multivariate curve resolution (MCR) method,^[26,34–38] factor analysis (FA),^[39–44] and fitting analysis.^[45] Such as the FA method, it is assumed that the hydration structures are same in some concentration region. Adopting this hypothesis, a single hydration shell spectrum was obtained. FA method deduced only one spectrum of perturbed water in the whole concentration region of aqueous salts.^[43,44] In fact, the assumptions have

been disputed. For instance, the hydration shell of organic compounds and ions^[9,46] were different in different concentration of solutes. MCR method^[26,34–38] assumed that hydration structures kept consistent in sufficiently low concentration region. For example, the hydration shell was thought to be unchanged below 1 M concentration of alkali halide aqueous solutions,^[26] and below 1–5 wt % concentration of some organic solutions.^[34] A single hydration spectrum was obtained in such low concentration regions. Recently, the MCR was developed to much higher concentration region,^[47,48] and it was used to deduce the concentration dependent spectra of hydration shell. These spectra were used to reflect the aggregation of solutes in higher concentration region.

In this work, the Raman spectra of some aqueous solutions in various concentrations were recorded in the OH stretching region. We proposed a new method based on the ratio spectra to obtain

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the spectra of hydration shell. None of the assumptions were employed in this method. Employing the Raman ratio spectrum, the spectrum of hydration-shell was obtained in each concentration. It was found the hydration spectra were different in every concentration, even in diluted concentration region. Using the hydration spectra, the hydration structures, the strength of hydrogen bonds, the number of water molecules in hydration shell of ions and organic molecules were obtained in their aqueous solutions.

Experimental section and MD simulations

Raman spectroscopy

NaCl (>99.0%) was purchased from Alfa Aesar. NaNO₃ (>99.0%), NaSCN (>98.5%), NaClO₄·H₂O (>99.0%), and Na₂SO₄ (>99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. The salt Na₂SO₄ had been heated at 650 °C for 8 h to remove the impurities. Other salts were used without further processing. Acetone-D₆ was bought from Sigma Aldrich. Deionized water was prepared from a Milli-Q reference system (Millipore, Bedford, MA, 18.4 MΩ·cm). All aqueous solutions were prepared by weight.

The Spontaneous Raman setup was described in previous works.^[49–52] The setup was described briefly here. A cw laser (Coherent, Verdi V5, 532 nm) with 4.0 W power was used to excite the solutions. Its polarization was purified by a Glan prism, and was controlled by a half wave plate. The Raman scattering light was collected at 180° geometry relative to the direction of laser. The polarization of the Raman light was selected by a Glan prism, and then scrambled by a depolarizer. The light was dispersed by the triple monochromator (Acton Research, TriplePro), and was record by a liquid-nitrogen-cooled CCD detector (Princeton Instruments, Spec-10:100B). The aqueous solutions were hold in a SiO₂ cuboid cell (1 cm × 1 cm × 3 cm). The temperature of the solutions was kept at 25 °C by a heating bath (THD-2006, Ningbo).

MD simulations

MD simulations were carried out to analyze the hydration structures of aqueous NaNO₃ and acetone, and the theoretical results are compared with those from Raman spectra. The all-atom Optimized Potential for Liquid Simulations (OPLS/AA) were chosen as force field^[53]. Lennard–Jones (LJ) parameters and atomic point charges for acetone were taken from <http://virtualchemistry.org>^[54,55]. For the nitrate ion, the LJ parameters and atomic point charges^[56,57] were used. The periodic boundary condition was used, and the unit cube contained 500 water molecules and a single solute, corresponding to concentration ~0.1 M. All the simulations were performed under the NPT ensemble, with the temperature and external pressure fixed at 300 K and 1 atm, respectively. Temperature and pressure were controlled by the Nosé–Hoover thermostat^[58] and Berendsen barostat^[59], respectively. A cutoff of 1 nm was used for the LJ interactions, and the long-range electrostatic interactions were treated by the slab-adapted Ewald sum method^[60]. The simulation for each system was carried out for 40 ns with a step of 2 fs.

Results and discussion

Hydration spectra from Raman ratio spectra

The spectrum of hydration shell, which is important to reflect the structure and dynamics of water molecules in hydration shell, has

been extracted from the spectra of the solutions through lots of methods. The popular methods are FA and MCR. Both methods are based on the matrix analysis. Taking MCR for example, the spectra of solutions with a series of concentrations were used to build a spectra matrix **D**. This matrix was decomposed into the concentration matrix **C** of the components in solutions and the spectra matrix **S** of corresponding components.^[26,36,61–63]

$$\mathbf{D} = \mathbf{C}\mathbf{S} \quad (1)$$

Aqueous solutions contain the solute molecules, the water molecules in hydration shell and in bulk water. Hence the total spectral matrix **D** are the sum of the spectral matrix of the three components. The matrix **D** is represented as the following equation.^[36]

$$\mathbf{D} = \mathbf{C}_{\text{bulk}}\mathbf{S}_{\text{bulk}} + \mathbf{C}_{\text{hydration}}\mathbf{S}_{\text{hydration}} + \mathbf{C}_{\text{solute}}\mathbf{S}_{\text{solute}} \quad (2)$$

Without the expression of matrix, the spectra of solution at each concentration can also be represented as the linear combination of the spectra of solute, water in bulk water and hydration shell.

$$I_{\text{solution}}(\nu) = I_{\text{bulk}}(\nu) + I_{\text{hydration}}(\nu) + I_{\text{solute}}(\nu) \quad (3)$$

In which, *I* is the spectral intensity, *ν* is the frequency. The spectrum of bulk water in solutions is proportional to that of pure water. Hence Eqn (3) is written as the following equation:

$$I_{\text{solution}}(\nu) = AI_{\text{pure}}(\nu) + I_{\text{hydration}}(\nu) + I_{\text{solute}}(\nu). \quad (4)$$

In which, *A* is a coefficient less than 1. As the OH stretching band (2800–3700 cm⁻¹) is very sensitive to the micro-structure of aqueous solutions, the spectra in this region were usually employed to study the aqueous solutions.^[27,49] Previous MCR method^[26] demonstrated the water molecules in hydration shell did not contribute to the spectra below ~3100 cm⁻¹. This is because some OH stretching vibrational coupling could produce the in-phase vibration below 3100 cm⁻¹ in bulk water; however the strong vibrational coupling does not occur in the spectra of hydration shells. Consequently in this region the above equation can be simplified into the following equation.

$$I_{\text{solution}}(\nu < 3100) = AI_{\text{pure}}(\nu < 3100) + I_{\text{solute}}(\nu < 3100) \quad (5)$$

Most of the inorganic salts, such as NaCl, NaNO₃, NaClO₄, and so on, do not contribute the spectra in the OH stretching region; thus, the above equation can further be simplified into the following equation.

$$I_{\text{solution}}(\nu < 3100) = AI_{\text{pure}}(\nu < 3100) \quad (6)$$

According to this equation, the coefficient *A* could be calculated.

$$A = I_{\text{solution}}(\nu < 3100)/I_{\text{pure}}(\nu < 3100) \quad (7)$$

To obtain the coefficient, the Raman ratio spectrum *R*(*ν*) is defined as the ratio of the spectrum of solution to that of pure water.

$$R(\nu) = I_{\text{solution}}(\nu)/I_{\text{pure}}(\nu) \quad (8)$$

According to Eqn (7), the intensity of *R*(*ν*) is the constant *A* below 3100 cm⁻¹.

The coefficient *A* from *R*(*ν*) can be employed to deduce the spectrum of water in hydration shell.

$$I_{\text{hydration}}(\nu) = I_{\text{solution}}(\nu) - AI_{\text{pure}}(\nu) \quad (9)$$

In this study, we employed Raman ratio spectrum to calculate the spectrum of hydration water in aqueous NaCl solution. Figure 1a shows the Raman spectra of pure water and the diluted aqueous

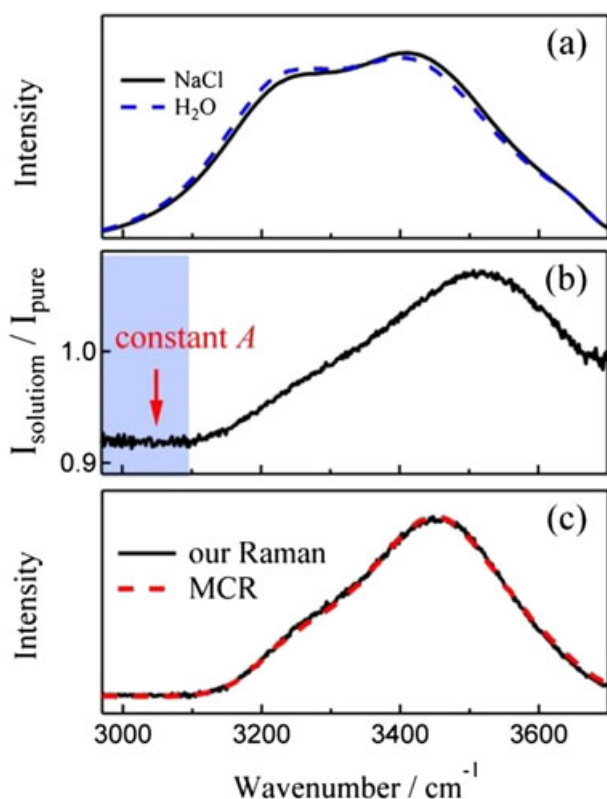


Figure 1. (a) Raman spectrum of OH stretching vibration region of pure water (dotted line) and NaCl solution (solid line); (b) the corresponding ratio spectrum; (c) the corresponding hydration spectrum from this Raman study (solid line) and from MCR^[26] (dotted line); the concentration of NaCl solution is 0.5 M.

NaCl solution (0.5 M) in the OH stretching region. Both spectra overlap seriously with each other. Employing Eqn (8), the Raman ratio spectrum was obtained, as shown in Fig. 1b. The intensity of the ratio spectrum is indeed constant below 3100 cm^{-1} . This constant value is the coefficient A . The value was employed to calculate the spectrum of water in hydration shell, which was shown in Fig. 1c. This spectrum agrees with that from MCR method.^[26] Thus, the Raman ratio spectra are feasible to extract the spectra of water in hydration shell from the spectra of aqueous solutions. The hydration spectrum mainly came from the water molecules in the hydration shell of anions.^[12,14,15,27,64–66]

Different from the aqueous inorganic salts, the spectra of the hydration shell of organic compounds in water cannot be obtained directly from the Raman ratio spectra. As the alkyl stretching vibration contributes below 3100 cm^{-1} region, a constant value is absent in the Raman ratio spectrum. Taking acetone in water for an example, the CH_3 stretching vibration of acetone contributes a little below 3100 cm^{-1} (Fig. 15a). This Raman band is amplified in the Raman ratio spectrum, and a constant value is not observed below 3100 cm^{-1} (Fig. 15b). While deuterated acetone (acetone-D₆) was used, the CH_3 stretching bands are removed from $\sim 3100\text{ cm}^{-1}$ (Fig. 2a). A constant value is observed below 3100 cm^{-1} in the ratio spectrum (Fig. 2b). Using the average intensity below 3100 cm^{-1} , the spectrum of water in the hydration shell of acetone-D₆ was calculated, as shown in Fig. 2c. In this spectrum, two bands centered at $\sim 3257\text{ cm}^{-1}$ and $\sim 3450\text{ cm}^{-1}$ are observed. Both bands were also recorded in the spectrum of water in the hydration shell of acetone in water from MCR method.^[34] In a word, in aqueous deuterated

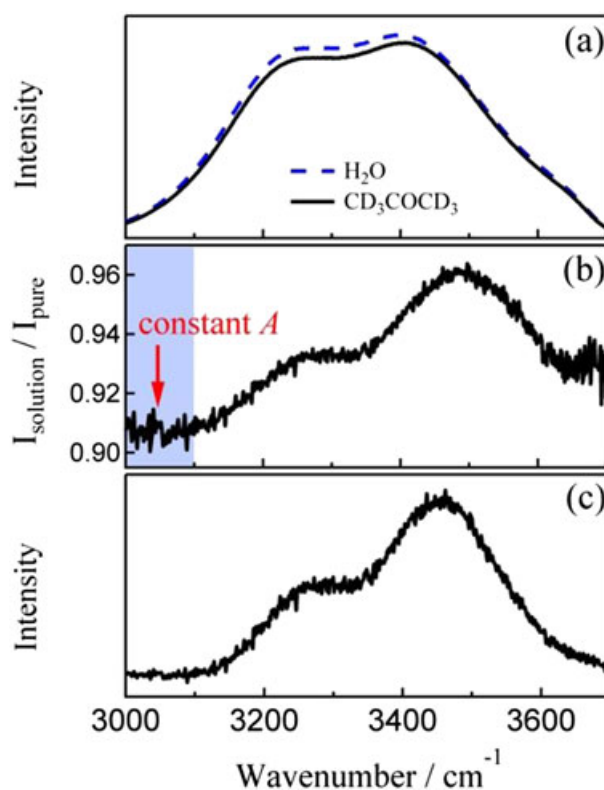


Figure 2. (a) Raman spectrum of pure water (dotted line) and aqueous deuterated acetone solution (solid line); (b) the corresponding Raman ratio spectrum; (c) Raman spectrum of hydration shell of deuterated acetone; The mole fraction of acetone is 0.02.

organic compounds, the spectra of the hydration shell can be directly obtained through the Raman ratio spectrum.

Comparing the previous FA,^[43,44] our Raman ratio spectra method avoids the hypothesis that the spectra of the hydration shell are same in the solutions with different concentrations. Employing the Raman ratio spectra, a single spectrum of the hydration shell is obtained in each concentration. The independent spectra reflect the particular micro-structure of the hydration shell in each concentration. Hence, the Raman ratio spectra can be employed to study the micro-structures in the aqueous solutions with different concentrations. The Raman ratio spectra have another advantage, that it is simpler than FA and MCR method. On the other hand, the Raman ratio spectrum has shortcomings. For example, this method cannot be applied to study the hydration shell of alcohols in water, as the OH vibrational band of alcohol overlaps seriously with that of water. However, the MCR method can be employed to study aqueous alcohols.^[37,38]

Structure of hydration shell of anions in water

The Raman spectra of diluted aqueous Na_2SO_4 , NaCl, NaSCN, NaNO_3 , and NaClO_4 solutions (0.1 M) were recorded in the OH stretching region, as shown in Fig. 3 a1–a5. Because the concentrations are small, all the Raman spectra are similar with the spectra of water. Figure 3 b1–b5 show the corresponding Raman ratio spectra. A constant value is observed in each Raman ratio spectra below 3100 cm^{-1} . Through employing the constant value, the spectra of the hydration shells of the anions were obtained, as shown in Fig. 3 c1–c5. These spectra are different with each other. This means the structures of the hydration shells of these anions are different.

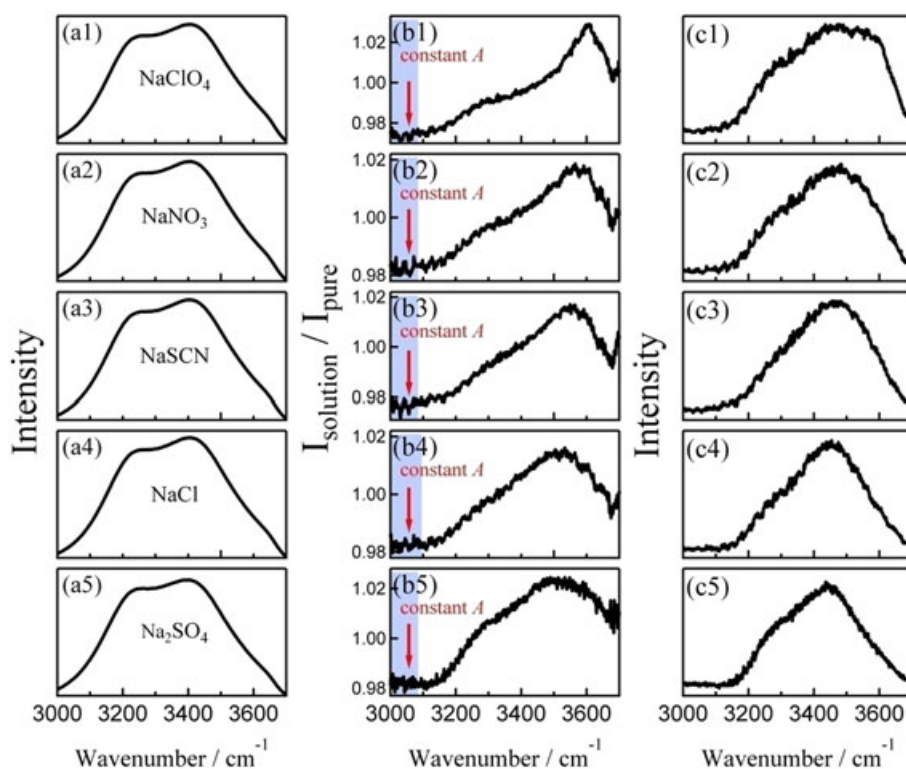


Figure 3. The Raman spectra of –OH stretching vibration region (a), the Raman ratio spectra (b) and Raman spectrum of hydration shell (c) of SO_4^{2-} , Cl^- , NO_3^- , SCN^- , and ClO_4^- in the sodium salt solutions; the concentration of these solutions is 0.1 M.

Taking the ClO_4^- and SO_4^{2-} for example, both anions are tetrahedral structure, but their spectra of the hydration shells are very different. A shoulder at high frequency region is observed obviously in the spectrum related to ClO_4^- (Fig. 3 c1); however the shoulder is absent in the spectrum related to SO_4^{2-} (Fig. 3 c5). This may be due to two distinct sub-shells in the first hydration shell of the ClO_4^- , which was confirmed by the a Car–Parrinello MD study.^[67]

The molecular interaction between water and anions can be reflected through the spectra of the hydration shell. For these asymmetry spectra, the first moment is applied to represent the mean frequency of the OH stretching frequency distribution.^[68,69] For different anions, the mean frequency shifts from 3420 cm^{-1} to 3445 cm^{-1} with the sequence of $\text{SO}_4^{2-} < \text{Cl}^- < \text{SCN}^- < \text{NO}_3^- < \text{ClO}_4^-$, as shown in Fig. 4. It indicates that the anion–water intermolecular interactions turn weak with this sequence. This sequence is consistent with the Hofmeister series.^[70,71]

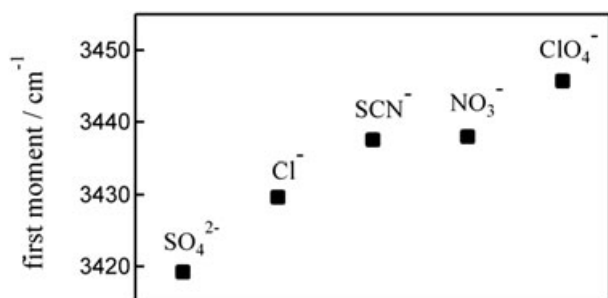


Figure 4. The first moment of Raman spectra of the hydration shell of SO_4^{2-} , Cl^- , SCN^- , NO_3^- , and ClO_4^- in the aqueous sodium salt solutions; the concentration of these solutions are 0.1 M.

Hydration number in diluted solutions

As mentioned above, the spectra of hydration shell can qualitatively reflect the structure of the hydration shell. Actually, the spectra can also be employed to quantitatively calculate the number of water molecules in the hydration shell. The hydration number $N_{\text{hydration}}$ can be represented as:

$$N_{\text{hydration}} = \frac{n_{\text{hydration}}}{n_{\text{solute}}} = \frac{n_{\text{hydration}}}{n_{\text{water}}} \bigg/ \frac{n_{\text{solute}}}{n_{\text{water}}} \quad (10)$$

In which, $n_{\text{hydration}}$, n_{water} , and n_{solute} are the total number of water molecules in hydration shell, all water molecules, and solutes in the aqueous solutions, respectively. $n_{\text{solute}}/n_{\text{water}}$ can be directly obtained from the concentration of the solutions. In aqueous solutions, all water molecules contain the water molecules in hydration shell and bulk water; thus

$$n_{\text{water}} = n_{\text{hydration}} + n_{\text{bulk}} \quad (11)$$

The numbers $n_{\text{hydration}}$ and n_{bulk} can be calculated from the integrated intensity of the corresponding spectra.

$$n_{\text{hydration}} = \frac{\int I_{\text{hydration}}(\nu) d\nu}{k\sigma_{\text{hydration}}} \quad (12)$$

$$n_{\text{bulk}} = \frac{\int I_{\text{bulk}}(\nu) d\nu}{k\sigma_{\text{water}}} \quad (13)$$

In which the $I(\nu)$ is the Raman spectra of water in the hydration shell or bulk, σ is the corresponding Raman scattering cross section, and k is a coefficient. Taking the Eqns (11), 12, and 13 into the Eqn (10), the hydration number can be expressed as:

$$N_{\text{hydration}} = \frac{\int I_{\text{hydration}}(v) dv}{\left(\int I_{\text{hydration}}(v) dv + \frac{\sigma_{\text{hydration}}}{\sigma_{\text{water}}} \int I_{\text{bulk}}(v) dv \right)} \bigg/ \frac{n_{\text{solute}}}{n_{\text{water}}} \quad (14)$$

The $\sigma_{\text{hydration}}$ does not equal to σ_{water} . For example, the ratio $\sigma_{\text{hydration}}/\sigma_{\text{water}}$ was determined to be 0.6, 1.1, 1.5, and 1.9 for F^- , Cl^- , Br^- , and I^- respectively.^[23] Here, the ratio also need to be calculated. The total water molecules in the aqueous solution can be calculated from water molecules in pure water with the same volume.

$$n_{\text{water}} = B \times n_{\text{pure}} \quad (15)$$

The parameter B can be calculated using the following equation.

$$B = \frac{\rho_{\text{mix}} M_{\text{H}_2\text{O}}}{(M_{\text{solute}} \chi / (1 - \chi) + M_{\text{H}_2\text{O}}) \rho_{\text{pure}}} \quad (16)$$

The derivation of B is put in appendix part. In this equation, χ is the mole fraction of solute in aqueous solution, ρ_{mix} and ρ_{pure} is the density of aqueous solution and pure water respectively, and M_{solute} and $M_{\text{H}_2\text{O}}$ are the molecular weight of solute and water molecules respectively.

According to Eqn (11) and Eqn (15), thus

$$B \times n_{\text{pure}} = n_{\text{hydration}} + n_{\text{bulk}} \quad (17)$$

The number of water molecules in pure water can be calculated according the following equation,

$$n_{\text{pure}} = \frac{\int I_{\text{pure}}(v) dv}{K \sigma_{\text{water}}} \quad (18)$$

Taking Eqns (12), (13), (18) into 17, we obtained the equation.

$$B \times \frac{\int I_{\text{pure}}(v) dv}{K \sigma_{\text{water}}} = \frac{\int I_{\text{hydration}}(v) dv}{K \sigma_{\text{hydration}}} - \frac{\int I_{\text{bulk}}(v) dv}{K \sigma_{\text{water}}} \quad (19)$$

Thus the $\sigma_{\text{hydration}}/\sigma_{\text{water}}$ can be calculated as:

$$\frac{\sigma_{\text{hydration}}}{\sigma_{\text{water}}} = \frac{\int I_{\text{hydration}}(v) dv}{\int B^* I_{\text{pure}}(v) dv - \int I_{\text{bulk}}(v) dv} \quad (20)$$

Using the Raman spectra of water and aqueous salt solutions (0.1 M), the corresponding spectra of the hydration shell, the ratio $\sigma_{\text{hydration}}/\sigma_{\text{water}}$ was determined to be 0.97 ± 0.02 , 0.99 ± 0.02 , and 1.20 ± 0.02 for NO_3^- , SO_4^{2-} , and Cl^- in aqueous sodium salts solution, and it is found the values didn't change with solution concentrations. The value for Cl^- agreed well with recent result.^[23] For aqueous acetone-D6 solution (mole fraction 0.01), the ratio $\sigma_{\text{hydration}}/\sigma_{\text{water}}$ was determined to 0.96 ± 0.02 .

Employing the Raman scattering cross sections, the hydration number of these solutes in water was obtained with the Eqn (14). All the $N_{\text{hydration}}$ are listed in Table 1. The hydration number of SO_4^{2-} is determined to be 12 ± 0.2 . The value agreed well with the average value 11 in the first hydration shell of SO_4^{2-} from previous MD simulation.^[72] The hydration number of Cl^- is determined to be 8.4 ± 0.1 . It also agreed well with 8.2 in the first hydration shell of Cl^- solutions from previous MD simulations.^[19] Thus the hydration number from the Raman spectra should be the number of water molecules in first hydration shell. The spectra of the hydration shell from Raman ratio spectra should be the spectra of the first hydration shell. The value for NO_3^- and acetone is determined by our MD simulations to be 11.4 ± 0.1 and 2.1 ± 0.3 , respectively, which were not reported in previous study.

Table 1. The hydration number of NO_3^- , SO_4^{2-} , Cl^- , and acetone-D6

Solution	Raman*	MD
SO_4^{2-}	12.0 ± 0.2	11 ^[72]
Cl^-	8.4 ± 0.1	8.2 ^[19]
NO_3^-	11.4 ± 0.1	11.3 ± 0.6
Acetone-D6	2.1 ± 0.3	2.1 ± 0.3

* The errors represent experimental standard deviations.

In MD simulations, the micro-structure around solutes in aqueous solutions can be described by radial distribution functions (RDF, $g(r)$) of the atom of water with the atom of solute. The number of water molecules in the first hydration shell can be calculated by integrating the $g_{ij}(r)$ from zero to the point at the first minimum of $g_{ij}(r)$.

$$N_{\text{hydration}} = 4\pi \rho_j \int_0^{r_{\text{min}}} g_{ij}(r) r^2 dr \quad (21)$$

where ρ_j is the number density of the j th solvent component.^[73]

Figure 5a shows the RDF between the oxygen atom of water molecules and the nitrogen atom of NO_3^- . The RDF shows a minimum at 4.45 Å. Integration of the RDF gives the 11.3 ± 0.6 water molecules in the first hydration shell of NO_3^- . This value agrees well with the number 11.4 ± 0.1 from Raman spectra, which are listed in Table 1. Consequently, the number of the water molecules from Raman ratio spectra should be the number of water molecules in the first hydration shell of anions in water. In acetone/water solution, the strong intermolecular interactions usually occur between the water molecules with the oxygen atom of acetone. The water molecules around the methyl groups interacted weakly with the methyl groups; thus, its spectra may be similar with the spectra of bulk water. Hence then, using this Raman ratio spectra, we may resolve the water molecules around the C=O group from bulk water and the hydration shell of methyl groups. The RDF of the atoms is plotted in Fig. 5b. Integration of the RDF deduces 2.1 ± 0.3 water molecules in the first hydration shell of oxygen atom of acetone. This value agrees with the Raman data 2.1 ± 0.3 . Hence, the number from Raman ratio spectra of aqueous acetone-D6 is

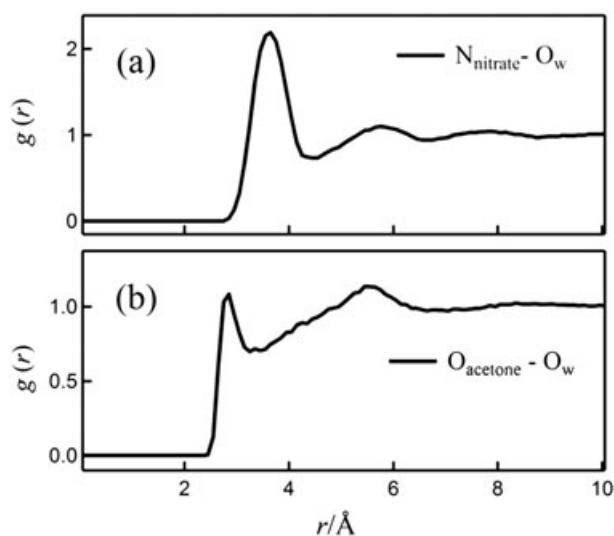


Figure 5. (a) The RDF between the oxygen of water and the nitrogen of NO_3^- , (b) RDF between the oxygen atoms of water and acetone.

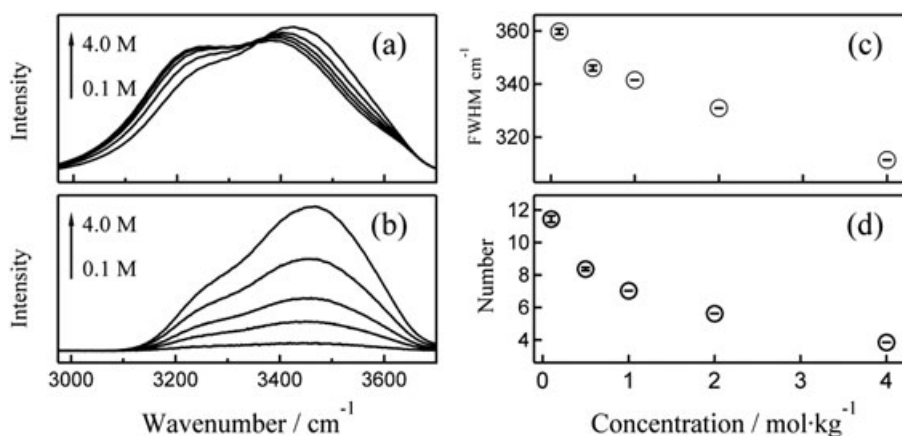


Figure 6. Raman spectra of NaNO₃ aqueous solutions (a) and the corresponding spectra of the hydration shell of NO₃⁻ (b) in OH stretching vibration region; (c) concentration-dependent full width at half maximum of the hydration spectra; (d) Concentration-dependent hydration number of NO₃⁻. The errors represent experimental standard deviations.

indeed the number of water molecules in the first hydration shell of the oxygen atom of acetone.

Hydration number and the micro-structure in concentrated solutions

As the spectra of hydration-shell can be obtained in each concentration, the hydration structure and the hydration number can be obtained in each concentration. The Raman spectra of aqueous NaNO₃ solutions with five concentrations were recorded in the OH stretching vibration region (Fig. 6a). Employing the Raman ratio spectra at each concentration (Fig. 2S), the corresponding spectra of the hydration shell were obtained (Fig. 6b). All the spectra were different with each other. Figure 6c shows the full width at half maximum (FWHM) of these hydration spectra. The FWHM increases with decreasing the concentration. Even below 1 M concentration, the FWHM is changed, which demonstrates that the structure of first hydration shell should be different in such diluted concentration region. The change of the hydration spectra should be ascribed to the aggregation of cations and anions. The decreasing FWHM suggested that the water molecules around anion were retarded with increasing the concentration, which was similarly observed by the ultrafast spectroscopy.^[11,12]

The contacted ion pairs (CIP), one kind of the aggregation, should be directly observed through the hydration number. The number of the water molecules in the first hydration shell of anions that from CIP should be smaller than that of free anions. The hydration numbers of NO₃⁻ were calculated through the hydration spectra and plotted in Fig. 6d. The decreasing of hydration number demonstrated that Na⁺ and NO₃⁻ aggregated into CIP with increasing the concentration of salt. The similar concentration dependent hydration numbers were also observed in some theoretical calculations,^[74,75] and the population of ion pairs were also observed to be increased with increasing the concentration in previous micro-Raman spectra of NaNO₃ droplets.^[1] The hydration number at the concentration 0.1 M of aqueous NaNO₃ agrees with the hydration number of free NO₃⁻ from MD; thus, CIP is absent in the diluted concentration. At the concentration 4 M, the hydration number is 4, is much smaller than the hydration number of free NO₃⁻. Consequently, larger clusters formed in the concentrated solutions.

Conclusions

In this study, we recorded the Raman spectra of many aqueous inorganic salts solutions and organic solutions in the O—H stretching vibration region. The Raman ratio spectra were first proposed to be employed to extract the spectra of the hydration shell of the solute in water. The Raman ratio spectra were obtained through dividing the Raman spectra of aqueous solutions from the spectrum of water. A constant value below 3100 cm⁻¹ region was observed in each Raman ratio spectrum in each concentration. The cut-off 3100 cm⁻¹ implies the hydration-shell spectrum has a negligible intensity below 3100 cm⁻¹. This constant value was applied to deduce directly the spectra of the hydration shell for aqueous NaCl, NaNO₃, NaClO₄, NaSCN, and Na₂SO₄ solutions, and aqueous acetone-D₆ solution.

Comparing the spectral shape of the hydration shell for SO₄²⁻, Cl⁻, NO₃⁻, SCN⁻, and ClO₄⁻ in their 0.1 M solutions, it was found that the structures of the hydration shell of these anions were very different. The mean frequencies of the spectra were in the sequence of SO₄²⁻ < Cl⁻ < SCN⁻–NO₃⁻ < ClO₄⁻, which demonstrated the anion water interactions turn weak with the same sequence, and this sequence is similar to the Hofmeister series. The spectra of the hydration shell was employed to quantitatively calculate the number of water molecules in the first hydration shell of NO₃⁻, SO₄²⁻, Cl⁻, and acetone-D₆ molecules. These numbers from Raman spectra were supported by the numbers of water molecules in the first hydration shell from molecular dynamic simulations. The spectra of the hydration shell of NO₃⁻ from diluted solution to concentrated solution were employed to study the structures of the hydration shell. It was found the number of water molecules in the first hydration shell decreased from 11 to 4 from 0.1 M to 4 M. The concentration dependent number demonstrated the ion pairs formed in this concentration region. The ion pairs exist even below the concentration 1 M, and larger clusters present in the concentrated solution (4 M).

Appendix

In pure water with the volume V , the number of water molecules (n_{pure}) can be calculated according to the density of pure water (ρ_{water}) and the molar weight of water molecule.

$$n_{\text{pure}} = \frac{V\rho_{\text{water}}}{M_{\text{water}}} \quad (\text{A1})$$

In aqueous solutions with the same volume V , the number of water molecules (n_{water}) and solute molecules (n_{solute}) can be calculated according to the density of aqueous solution (ρ_{mix}) and the molar weight of solute (M_{solute}):

$$M_{\text{water}} * n_{\text{water}} + M_{\text{solute}} * n_{\text{solute}} = V\rho_{\text{mix}}. \quad (\text{A2})$$

The number of water molecules (n_{water}) and solute molecules (n_{solute}) can be connected with the mole fraction of solute (χ).

$$n_{\text{solute}} = n_{\text{water}} * \frac{\chi}{1 - \chi} \quad (\text{A3})$$

Using the above equation, n_{water} can be expressed as:

$$n_{\text{water}} = \frac{V\rho_{\text{mix}}}{M_{\text{solute}}\chi / (1 - \chi) + M_{\text{water}}}. \quad (\text{A4})$$

Taking the Eqns (A1) and (A4) into the Eqn (15), the parameter B can be represented as

$$B = \frac{\rho_{\text{mix}} M_{\text{water}}}{[M_{\text{solute}}\chi / (1 - \chi) + M_{\text{water}}] \rho_{\text{water}}}. \quad (\text{A5})$$

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