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## MOLECULAR SPECTROSCOPY

# The Effect of Hydration of Ions of Inorganic Salts on the Shape of the Raman Stretching Band of Water

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**Abstract**—The shape of the Raman stretching band of water molecules in aqueous solutions of electrolytes KBr, KCl, KI, NaCl, and NaI is studied. It is confirmed that the characteristics of the stretching band strongly depend on the concentration and type of salt. The behavior of different parameters of the band is explained in terms of the theory of hydration of salts. © *2005 Pleiades Publishing, Inc.*

## INTRODUCTION

Many authors [1–9] have attempted to theoretically explain the particular features of the Raman spectra of water molecules and their dependences on various parameters of a medium (temperature, concentration of dissolved impurities) in the expectation that ascertaining the nature and mechanisms of formation of these spectra can provide information useful in studying the structure of water. The study of the Raman spectra of water and the efforts to construct a model reflecting as fully as possible the dependences of these spectra on the parameters of a medium are stimulated not only by fundamental problems of physics of liquid water, but also by applied tasks of creating new methods for determining different parameters of aqueous media [10].

Unfortunately, only limited success has been achieved in this field: no model has been constructed of vibrational processes in the system of bound molecules of liquid water that could unambiguously account for the dependence of the shape of the Raman bands on different parameters of a medium, the occurrence of the relationship between the stretching and bending bands (the Fermi resonance) [1] has not been ascertained, the interactions between the molecules of impurity and water have not been investigated, and so on.

In this study, we will attempt to explain in the context of the hydration theory [11, 12] some dependences of the parameters of the Raman stretching band of water on the type and concentration of ions dissolved in it.

The characteristics of the Raman stretching band of water in relation to the concentration of dissolved salts and acids were studied in [4, 7–9] and other publications. Here, we will study similar dependences but in a larger range of concentrations, paying special attention to the occurrence of deviations from linearity in the concentration dependences of the chosen parameters of the stretching band and comparing them with known characteristics of hydration.

## METHODS OF STUDY

As an object of study, we chose aqueous solutions of alkali halide salts with the cations $Na^+$, $K^+$, and $NH_4^+$ and the anions $F^-$, $Cl^-$, $Br^-$, and $I^-$. We used high purity grade and reagent grade salts. The concentrations of the salts in the solutions were varied within the following ranges: 0–4 M (KBr), 0–4 M (NaCl), 0–6 M ($NH_4Cl$), 0–3.6 M (KCl), 0–10 M (NaI), 0–15 M ($NH_4F$), and 0–8 M (KI). These ranges were chosen on the basis of the solubility of these salts in water at room temperature (25°C).

To perform a detailed analysis of the dependence of the shape of the Raman stretching band of water on the concentration of a salt dissolved in water, the step of variation in the concentration was chosen as small as possible: in the range of concentrations of up to 3 M, the step was no greater than 0.3 M and, on further increase in concentration, the step was continuously increased, but to a value not exceeding 1 M.

As a source of exciting light in our experiments, we used radiation of an LG-106-*M1* argon laser at the wavelength $\lambda = 488$ nm. The lasing power at this wavelength amounted to about 200 mW; the laser radiation was vertically polarized. Raman radiation scattered at an angle of 90° was focused on the entrance slit of an OMA-1 multichannel analyzer (Princeton Applied Research Corporation) with a diffraction grating of 550 lines/mm, which ensured the parallel detection of the spectral range with a width of 70 nm with a resolution of 0.14 nm/channel (at a slit width of 25 μm).

In the course of the experiments, the solutions were maintained at a temperature of 24.7°C; the change in the temperature of a cell (with a volume of 20 ml) during the recording of the spectrum did not exceed 0.2°C. The heating of the sample by laser radiation and the temperature gradient inside the cell were ignored, since, according to estimates, their effect on the measurement results was negligibly small.

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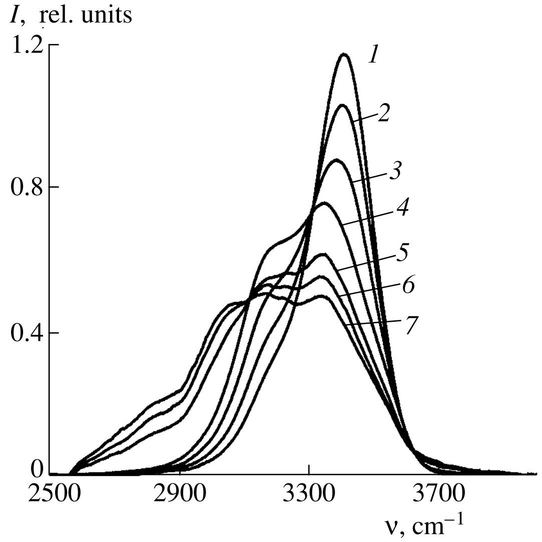

**Fig. 1.** Raman stretching band of water in solutions of electrolytes at different salt concentrations: (*1*) 6 M of NaI, (*2*) 4 M of NaI, (*3*) 2 M of NaI, (*4*) distillate, (*5*) 7 M of $NH_4F$, (*6*) 12 M of $NH_4F$, and (*7*) 7 M of $NH_4F$.

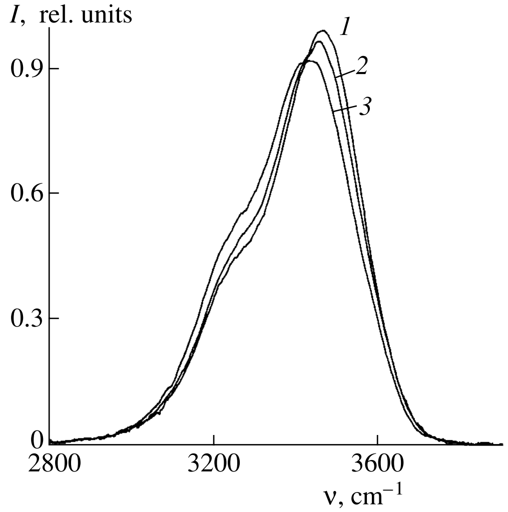

**Fig. 2.** Raman stretching band of water in solutions of potassium salts (at a concentration of 3.2 M): (*1*) KI, (*2*) KBr, and (*3*) KCl.

## RESULTS AND DISCUSSION

As an example, Fig. 1 shows the Raman stretching band of water in solutions with different concentrations of the salt NaI. It is seen from this figure that, as the concentration of NaI increases, the maximum of the spectral band shifts toward higher frequencies, the intensity of the high-frequency shoulder increases, while that of the low-frequency one decreases. In addition, the band narrows with increasing concentration. The Raman stretching band of water in the aqueous solutions of the salts KBr, KCl, KI, NaCl, and NaI behave in a similar manner. These results agree with data in the literature [7–10].

A different behavior of the Raman stretching band of water was observed upon changing the concentration of the salts of ammonium (Fig. 1). As is seen from this figure that, as the concentration of the solution of $NH_4F$ increases, the position of the maximum of the spectral band does not change, the intensity of the high-frequency shoulder decreases, while that of the low-frequency one increases. Furthermore, an additional band appears in the low-frequency range. We explain such a behavior of the Raman spectrum of water in the aqueous solution of $NH_4F$ by the specific structure of the $NH_4^+$ and $F^-$ ions, which manifests itself in their hydration (see below).

As was indicated above, the shape of the Raman stretching band of water depends not only on the concentration of a salt dissolved in it, but also on the type of this salt. Figure 2 presents the Raman stretching band of water in the spectra of salt solutions of the same concentration (3.2 M) with different anions and the same cation, $K^+$. The dependences of the position of the maximum $\nu_{max}$ and the half-width $\Delta\nu$ of the stretching band on the salt concentration are shown in Figs. 3 and 4, respectively. As is seen from these figures, for one and the same cation, the characteristics of the band in the spectra of the solutions with different anions are markedly different, whereas the replacement of one cation by some other cation hardly affect the characteristics of the band. It follows from this that the effect of the anions (except for the $F^-$ ion, see below) is substantially stronger than that of the cations.

To explain these data, we invoked the theory of hydration of ions. The weak effect of the cations on the stretching band in comparison with the effect of the anions can be explained by the asymmetric distribution of the charge in the dipoles of the water molecules. It is

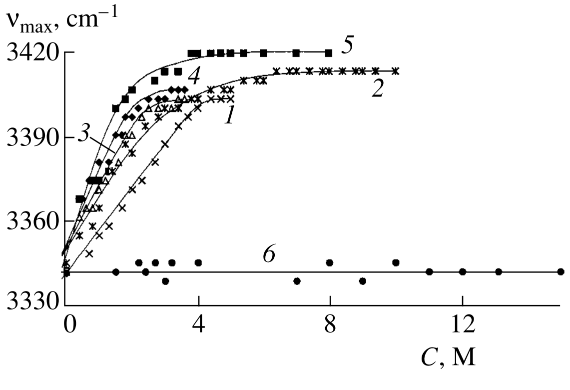

**Fig. 3.** Maximum of the Raman stretching band of water vs. concentration of different salts (the frequency of the band maximum is determined with an accuracy of ±3 cm$^{-1}$): (*1*) NaCl, (*2*) NaI, (*3*) KCl, (*4*) KBr, (*5*) KI, and (*6*) $NH_4F$.

known that, in the water molecules, the negative charge is displaced 0.25 Å toward the periphery [11], whereas the positive charge is concentrated closer to the central part of the molecule. Therefore, if the radius and the charge magnitude of a cation are equal to the corresponding parameters of an anion, the Coulomb cation–water interaction is stronger than the anion–water interaction. This means that the frequency of the stretching vibrations of the O–H bond of a water molecule in the hydration shell of a cation is lower than the vibrational frequency of the O–H bond of a water molecule in the hydration shell of an anion of the same size and charge magnitude. Furthermore, the majority of anions are greater in size than cations, their charge density is smaller, and they bind water molecules much more weakly. That is why most anions are hydrated negatively (Table 1): in water, the strength of their interactions with water dipoles is weaker than the strength of hydrogen bonds between water molecules. As a result, the mobility of water molecules in the hydration shells of anions increases and the frequency of vibrations of the O–H bond increases. If, simultaneously, there are positively hydrated cations in water, the resultant effect will depend on the relation between the hydration forces of the anions and cations.

As is seen from Table 1, among the salt solutions under study, the $Na^+$ and $F^-$ ions are positively hydrated, while the $K^+$, $I^-$, $Br^-$, and $Cl^-$ ions are negatively hydrated. The anions affect the vibrations of the water molecules much more strongly than the cations, because the observed behavior of the Raman stretching band of water in the solutions (Figs. 1–4) is consistent with an increase in the fraction of water molecules with a higher frequency of vibrations of the O–H bonds.

If one arranges the anions in increasing order of their sizes, a series will be obtained: $F^- < Cl^- < Br^- < I^-$. On the basis of our experimental data (Figs. 2–4), a similar series can be composed with respect to the effect of the anions on the shape of the Raman stretching band of water. The greatest anion $I^-$ has the strongest effect on the stretching band.

The salt $NH_4F$ is an exception to this general pattern of the effect of the salts considered on the Raman stretching band of water. For this salt, the band maximum remains unchanged upon changing the concentration, and only the redistribution between the amounts of strongly and weakly bound water molecules takes place. This is consistent with the known properties of the $NH_4^+$ and $F^-$ ions. The ammonium ion is nearly tetrahedral in structure; it fits well into the structure of water and does not significantly change the bonds between water molecules. In contrast, the small-sized fluorine ion possesses the property of positive hydration; in water, it forms a hydration shell, in which water molecules are bound stronger than in pure water. Consequently, addition of the salt $NH_4F$ to water leads only to an increase in the number of strongly bound water molecules, virtually without changing the frequency of vibrations of the O–H bonds.

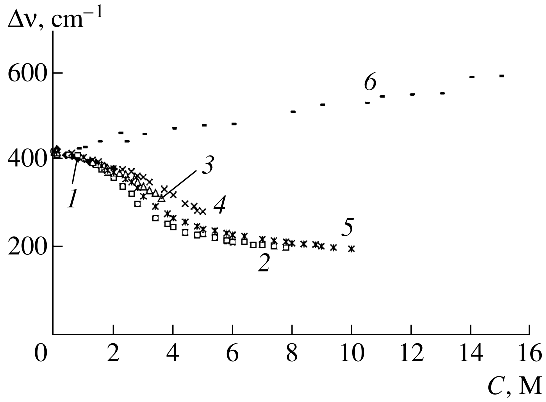

**Fig. 4.** Half-width of the Raman stretching band of water vs. concentration of different salts (the band half-width is determined with an accuracy of ±3 $cm^{-1}$): (*1*) KBr, (*2*) KI, (*3*), KCl, (*4*) NaCl, (*5*) NaI, and (*6*) $NH_4F$.

### *The Frequency Maximum of the Raman Stretching Band of Water in the Salt Solutions in Relation to the Concentration and the Type of the Dissolved Ions*

On the basis of the experimental data obtained for all the salts under study, in Fig. 3, we plotted the dependences of the maximum of the Raman stretching band of water versus the salt concentration, ($\nu_{max}(C)$).

For the aqueous solutions with one and the same salt concentration, the shift of the Raman stretching band of water in the solution of KI is greater than in the solutions of KBr and KCl. Therefore, we have the fol-

**Table 1.** Characteristics of ions (from the data in the literature)

| Ion | Type of hydration [13] | Charge | Mass, au | Radius, Å | Mobility at 18°C [13] |
|---|---|---|---|---|---|
| $Li^+$ | Positive | +1 | 7 | 0.68 | 33.0 |
| $Na^+$ | Positive | +1 | 23 | 0.98 | 43.3 |
| $K^+$ | Negative | +1 | 39 | 1.33 | 64.3 |
| $Rb^+$ | Negative | +1 | 85.5 | 1.49 | 67.6 |
| $Cs^+$ | Negative | +1 | 133 | 1.65 | 65.5 |
| $NH_4^+$ | Positive | +1 | 18 | 1.43 | 64.5 |
| $F^-$ | Positive | –1 | 19 | 1.33 | – |
| $Cl^-$ | Negative | –1 | 35.5 | 1.81 | 65.3 |
| $Br^-$ | Negative | –1 | 80 | 1.96 | 67.4 |
| $I^-$ | Negative | –1 | 127 | 2.20 | 66.3 |

**Table 2.** Concentrations $C_1$ and $C_2$ for the solutions under study

| Salt | Concentration $C_1$, M | Concentration $C_2$, M |
|---|---|---|
| KBr | 1.8 | 2.5 |
| KI | 1.3 | 2.4 |
| NaCl | 1.8 | 3 |
| NaI | 2.4 | 4.4 |
| $NH_4Cl$ | | 4.8 |

**Table 3.** Slopes of the straight lines $\chi_{12}(C)$ or the salt solutions under study

| Salt | Slope of the straight line $\chi_{12}(C)$ | Linearity range of $\chi_{12}(C)$ |
|---|---|---|
| KBr | $0.281 \pm 0.004$ | 1–4 M |
| KI | $0.448 \pm 0.004$ | 0.5–7.6 M |
| KCl | $0.181 \pm 0.002$ | 1–3.6 M |
| NaCl | $0.221 \pm 0.003$ | 0.5–4 M |
| NaI | $0.414 \pm 0.005$ | 1.5–7.6 M |
| $NH_4Cl$ | $0.121 \pm 0.002$ | 0–6 M |

lowing series of these anions with respect to their effect on the shape of the Raman stretching band of water: $Cl^- < Br^- < I^-$.

As is seen from Fig. 3, one can distinguish the following three ranges in the concentration dependence of the maximum of the Raman stretching band of water $\nu_{max}(C)$: in the range from 0 to ~1.5 M, the shift of the maximum linearly depends on the salt concentration; in the range from ~1.5 to ~2.5 M, this dependence is nonlinear; and, in the range $C > 2.5$ M, the position of the maximum does not depend on the concentration ($\nu_{max}(C)$ flattens out).

The occurrence of these three ranges in the dependence $\nu_{max}(C)$ can be explained in terms of the theory of hydration. Upon dissolving a salt in water, an ion forms a hydration sphere around itself (short- and long-range hydration zones in the Samoĭlov model [12]), which contains water molecules interacting with this ion. At small concentrations, the hydration spheres of the ions do not come in contact each other and the general number of water molecules interacting with the ions is proportional to the number of these ions in the solution. In diluted solutions, such interactions manifest itself in a linear concentration shift of the band maximum toward higher frequencies.

In the concentration range from ~1.5 to ~2.5 M, the zones of long-range hydration of different ions can contact and overlap each other. In this case, the solution does not contain volumes with an intact structure of water, but the dissolved ions still can break or weaken the hydrogen bonds between water molecules.

At concentrations $C > 2.5$ M, all the water molecules are involved in the short-range hydration process. A further increase in the salt concentration does not result in weakening or breaking of hydrogen bonds between water molecules; stable formations (short-range hydration shells) arise in the solutions. With a further increase in the solution concentration, the frequency of the band maximum remains unchanged.

From the dependences $\nu_{max}(C)$, we determined the values of the concentration $C_1$, at which $\nu_{max}(C)$ deviates from a linear dependence (the long-range hydration), and the values of the concentration $C_2$, at which this dependence levels off (the short-range hydration). In principle, knowing the concentrations $C_1$ and $C_2$, one can find the hydration numbers of the ions of the salts under study. The values of the concentrations $C_1$ and $C_2$ are presented in Table 2.

### *The Half-Width of the Raman Stretching Band of Water in the Salt Solutions in Relation to the Concentration and the Type of the Dissolved Ions*

In Fig. 4, the dependence of the half-width of the Raman stretching band of water in the solutions under study on the salt concentration $\Delta\nu(C)$ is presented. As is seen from this figure, as the concentration of a salt increases, the half-width of the Raman stretching band of water decreases differently depending on the type of the salt. The degree of decrease in the half-width corresponds to the same series $Cl^- < Br^- < I^-$ that manifested itself in the dependence $\nu_{max}(C)$.

The decrease in the half-width of the Raman stretching band of water with increasing salt concentration can be explained by an increase in the number of weakened or broken hydrogen bonds due to addition of ions. We note that the curve $\nu_{max}(C)$ behaves differently than the curve $\Delta\nu(C)$ (Figs. 3 and 4). The frequency of the maximum of the Raman stretching band of water flattens out in a concentration range greater than 2.5 M. The half-width of the spectra decreases steadily in the entire range of the concentrations under study. It is likely that this occurs because the shift of the band maximum toward higher frequencies is caused by the presence of hydrogen bonds in water that can be broken. When there are no such bonds (all the hydration spheres are ordered), the position of the band maximum remains unchanged. The half-width of the stretching band is determined by the occurrence of bonding of any type for the O–H groups (intermolecular, electrostatic, intramolecular valence, hydrogen, etc). When the hydration spheres are ordered, the width of the stretching band continues to decrease with increasing the ion concentration, because the fraction of the water molecules with weakened bonds continues to increase.

### *The Intensity Ratio of the High- and Low-Frequency Regions of the Raman Stretching Band of Water in Relation to the Concentration of the Dissolved Salts*

As a quantitative characteristics of the change in the shape of the Raman band 3000–3800 cm$^{-1}$ under the action of dissolved salts, we used the quantity $\chi_{12}$ equal to the intensity ratio of the high- and low-frequency regions of the band, $\chi_{12} = I(\nu_1)/I(\nu_2)$. The frequencies $\nu_1$ and $\nu_2$ corresponded to the critical points of the first derivative of the Raman stretching band of distilled water, which, in the calculations, were taken to be $\nu_1 = 3370$ cm$^{-1}$ and $\nu_2 = 3160$ cm$^{-1}$. The dependence of the parameter $\chi_{12}$ on the salt concentration was plotted in the concentration ranges under study. These calculations showed that, from 1–1.5 M to the maximal concentration of the salt solution, the dependence $\chi_{12}(C)$ can be approximated by a straight line for all the salts except ammonium fluoride, for which the parameter $\chi_{12}$ decreases nonlinearly with increasing concentration. The slope angles of the straight lines $\chi_{12}(C)$ in the corresponding concentration ranges of different electrolytes are presented in Table 3.

The data of Table 3 confirm once again that the anions and cations differently affect the Raman stretching band of water. The effect of the anions is much stronger and it increases in the series Cl$^-$, Br$^-$, and I$^-$. Within the measurement accuracy, we failed to determine a similar series for the cations with respect to the degree of their influence on the stretching Raman band.

## CONCLUSIONS

Our investigation of the shape of the Raman stretching band of water in aqueous solutions of electrolytes showed that the characteristics of this band substantially depend on the concentration and type of a salt dissolved. The behavior of different parameters of the band can be explained in the context of the theory of hydration of salts. However, our investigations do not describe the complete pattern of structural changes in the bulk of water occurring upon addition of different impurities to the water. To obtain maximum information, apart from studying the stretching band, it is necessary to study the low-frequency and bending Raman bands of water. These bands are assumed to be more sensitive to small changes in the concentration of impurities. In this respect, the low-frequency band is of special interest, since the changes in the concentration of impurities are likely to affect primarily the intermolecular vibrations. Therefore, in the future, we plan to study the entire Raman spectrum of water in solutions of organic and inorganic salts.

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