Revelation of Ion Hydration in Raman Scattering Spectral Bands of Water

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Abstract—The influence of ions with different hydration properties on the stretching, bending, and low-frequency bands of water Raman scattering spectra has been investigated. The obtained results are explained using the ion hydration theory: from the point of view of the formation of hydration shells, ion pairs and complexes, and the migration of protons in water. Using the detected peculiarities of the dependences of spectra characteristics on the salt concentration for the determination of the parameters of long-range and short-range hydration is proposed.

INTRODUCTION

The study of the processes of ion hydration and the determination of quantitative characteristics of the interaction of ions with water molecules is one of the fundamental problems of chemistry and the physics of solutions [1, 2]. It is known that the interaction of water molecules with ions of dissolved inorganic compounds provide changes in the vibrational characteristics of water molecules. Such changes reveal themselves in the Raman scattering (RS) spectra of water in solutions, in particular, in Raman low-frequency bands generated by the intermolecular interactions of water molecules, and in high-frequency bands generated by intramolecular interactions. In [3], using the characteristics of the water RS spectra stretching band to determine the hydration parameters was proposed. This method follows naturally from the results of numerous studies (e.g., [3–9]) in which the influence of some dissolved salts on the water RS stretching band was investigated.

In [3–9] and other studies, the influence of the salts of alkali metals on different spectral bands of water RS (primarily, on the stretching band), has been investigated. There are only several papers devoted to the study of the influence of the salts of bivalent [3] or trivalent [6] metals on the water RS stretching band. Unfortunately, the results presented in these papers do not allow one to obtain an adequate picture of the processes of the hydration of ions with different properties to make conclusions on the validity of any model of the water structure in solutions.

We have already presented the results of a study of the influence of sodium and potassium dissolved halides on the water RS stretching band [9]. It is known

that the cations of bivalent metals are hydrated in water more strongly than the cations of alkali metals, and that aluminum cations create ion pairs and complexes in water already at low salt concentrations. Halogen anions I⁻, Br⁻, and Cl⁻ are negatively hydrated, and sulphate anions are positively hydrated ions. Therefore, it was interesting to compare how ions with significantly different hydration properties appear with changes in the spectral characteristics of the water Raman stretching band, with bending and low-frequency bands, and to use this to determine the hydration parameters. To do so, the following has been made in this study:

(1) The row of salts studied in [9] was significantly expanded: a) LiI, LiBr, LiCl, NaBr, NaF, KF, CsI, and CsCl were added to the already investigated halides of sodium and potassium; and b) the influence of chlorides and sulphates of univalent, bivalent, and trivalent metals was investigated.

(2) To increase the accuracy of the determination of the parameters of the hydration of ions, the explored range of concentrations of salts was extended up to complete solubility, and the step for concentrations was reduced to 0.2–0.1 M.

(3) The influence of the halides of metals on the bending and low-frequency bands of the water RS spectra was investigated in the whole range of the solubility of salts.

1. EXPERIMENT

Our research objects were water solutions of salts with Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, and Al^{3+} cations, and F^-, Cl^-, Br^-, I^-, and SO_4^{2-} anions,

Intensity, arb. units
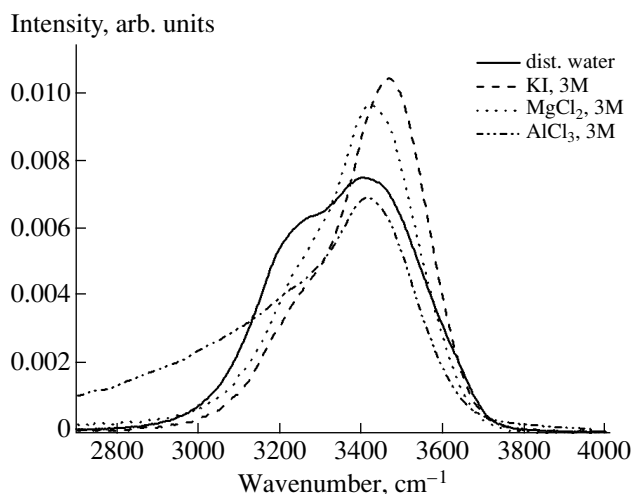
Fig. 1. Raman scattering stretching bands of water in the solutions of the chlorides of metals.

Fig. 2. Dependences of the frequency of the maximum of Raman scattering stretching band of water in solutions on the concentration of salts $\nu_{max}(C)$.

in the entire range of concentrations of their solubility. The concentration step was 0.1–0.2 M.

In the experiments on the analysis of the stretching band of the water RS spectra, the Raman scattering signal was excited by the radiation of an argon laser (wavelength $\lambda = 488$ nm, power of laser radiation about 600 mW). Diffused under the angle 90°, Raman radiation was collected on the input slit of the Optical Multichannel Analyzer OMA-1 polychromator (Princeton Applied Research Corporation) equipped with a grating of 550 lines per mm, which ensured the parallel detection of the 70-nm-wide spectrum range, with a resolution of 0.14 nm/channel (slit width 25 μ).

The bending band (in the region of 1654 cm^{-1}) and low-frequency band (in the region of 186 cm^{-1}) of the water RS spectra were recorded by an ISA/Jobin Yvon Raman S-3000 spectrometer. An argon laser (wavelength $\lambda = 488$ nm, power of laser radiation is about 1 Wt) was used as the source of exciting radiation. Scattered Raman radiation was recorded by triple monochromator and CCD camera. The spectral resolution of the receiver was 5 cm^{-1} (slit width 30 μ).

The Raman scattering spectra of water in the solutions were recorded at room temperature.

2. RESULTS AND DISCUSSION

2.1. Revelation of the Hydration of Ions in the Water Raman Stretching Band

Research on the revelation of the hydration of ions in the behavior of the water RS stretching band was carried out for three groups of inorganic salts contrasted in their hydration properties: halides of alkali metals, chlorides and sulphates of uni-, bi-, and trivalent metals. The cations of alkali metals fix the neig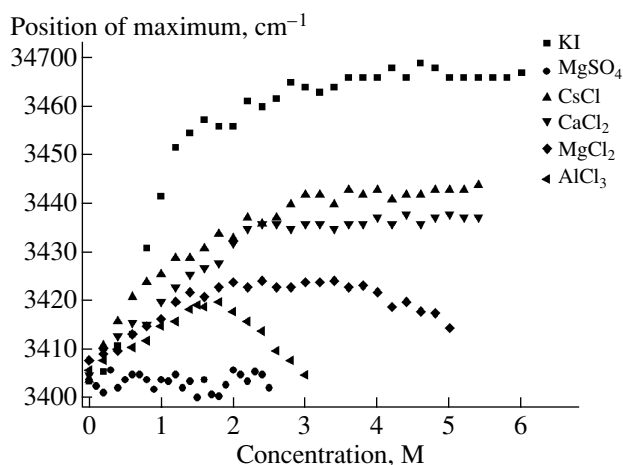hboring water molecules weaker than the cations of bi- and trivalent metals. All anions of halogens have small sizes, and they are negatively hydrated. Sulphate anions are large multiatomic complexes, and they are positively hydrated.

As was shown in [9] and other papers, the following properties for the solutions of the majority of salts are common: with an increasing concentration of salts dissolved in water, the intensity of the high-frequency region of the RS stretching band increases, and that of the low-frequency region decreases; the band shifts to higher frequencies, and the band width decreases (Fig. 1); the shape and the position of the stretching band depend on the concentration and the type of salt. However, the strength and peculiarities of the hydration of different groups of salts manifest themselves in these common laws differently.

2.1.1. Halides of alkali metals. In Fig. 2, the dependences of the position of the water stretching band maximum in the solutions of salts on salt concentration $\nu_{max}(C)$ are presented. The accuracy of the frequency determination is 3 cm^{-1}. As one can see from Fig. 2, the dependences $\nu_{max}(C)$ have three different ranges: the range of concentrations 0–1.5 M, where the shift of the band maximum is linearly dependent on the salt concentration; the range from 1.5 M to 2.0 M, where the dependence $\nu_{max}(C)$ is nonlinear; and the range with the concentration C > 2.0 M, where the position of the band maximum does not depend on the salt concentration ($\nu_{max}(C)$ flattens out). In [9], it was assumed that the existence of these three ranges in the dependence $\nu_{max}(C)$ could be explained by the establishment of the short-range and long-range hydration of ions. 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. At concentrations C > 2.5 M, all of the water molecules are involved in short-range hydration. Therefore, from the dependences $\nu_{max}(C)$, one can

Table 1. Values of the shift of the maximum of the water Raman scattering valence band towards high frequencies with an increasing concentration in the solutions of the halides of alkali metals

Salt	Range of concentrations studied	Maximum shift observed at concentrations:				C_{pl}:
		1 M	3 M	5 M	max. conc.	
LiI	0–9 M	27 cm^{-1}	61 cm^{-1}	65 cm^{-1}	65 cm^{-1}	3.4 M
LiBr	0–14 M	12 cm^{-1}	31 cm^{-1}	42 cm^{-1}	49 cm^{-1}	5.2 M
LiCl	0–12 M	9 cm^{-1}	31 cm^{-1}	40 cm^{-1}	42 cm^{-1}	5.0 M
NaI	0–9 M	33 cm^{-1}	63 cm^{-1}	65 cm^{-1}	65 cm^{-1}	3.2 M
NaBr	0–7 M	19 cm^{-1}	48 cm^{-1}	49 cm^{-1}	52 cm^{-1}	3.4 M
NaCl	0–5 M	11 cm^{-1}	28 cm^{-1}	37 cm^{-1}	37 cm^{-1}	3.6 M
KI	0–6 M	38 cm^{-1}	60 cm^{-1}	62 cm^{-1}	63 cm^{-1}	2.6 M
KBr	0–5 M	18 cm^{-1}	43 cm^{-1}	49 cm^{-1}	49 cm^{-1}	3.2 M
KCl	0–4 M	11 cm^{-1}	34 cm^{-1}	–	40 cm^{-1}	–
KF	0–13 M	1 cm^{-1}	11 cm^{-1}	16 cm^{-1}	–2 cm^{-1}	5 M–plateau
					15 cm^{-1}–plateau	8.4 M–downturn
CsI	0–3 M	28 cm^{-1}	60 cm^{-1}	–	60 cm^{-1}	2.2 M
CsCl	0–9 M	22 cm^{-1}	38 cm^{-1}	39 cm^{-1}	30 cm^{-1}	2.8 M–plateau
					39 cm^{-1}–plateau	7.8 M–downturn

determine the values of the concentrations, at which long-range and short-range hydration are established.

It was found that the value of the shift of the water RS stretching band maximum with an increasing concentration of alkali metal halides in the whole range of their solubility depends on the type of anions and does not depend on the type of cations (Table 1). The following series of anions with respect to their effect on the position of the maximum of the Raman stretching band of water takes place: $F^- < Cl^- < Br^- < I^-$. The value C_{pl} of the beginning of the plateau on the curve $\nu_{max}(C)$ depends both on anions and on cations. This value changes according to the following rows: $Cs^+ < Na^+ < Li^+$ for cations, and $I^- < Br^- < Cl^- < F^-$ for anions. For the solutions of KCl, the plateau is not formed because of the low solubility. Thus, the more negatively hydrated the ion is, the faster the processes of water molecule redistribution and the greater the changes in the vibrational characteristics of the water molecules; therefore, the greater the shift of the water Raman stretching band maximum in the solution of the corresponding salt with an increasing concentration, the smaller the value of C_{pl} at the beginning of the plateau on the curve $\nu_{max}(C)$. For the solutions of the fluorides of metals, there is no shift in the water Raman stretching band maximum, because the F^- anion is positively hydrated.

As can be seen from Fig. 2, the curve $\nu_{max}(C)$ for CsCl solutions has an unusual shape: at $C_{pl} = 2.4$ M, it enters the plateau and, at $C = 7.6$ M, it begins to turn down. We suppose that this downturn is explained by the formation of ion pairs in concentrated water solu-

tions of CsCl [10]. When ion pairs are formed, ion–ion interactions amplify; hydration shells become misshaped and shared by several molecules (first, noncontact ion pairs are formed; then, contact ion pairs), and water molecules become more bound. As a result, the maximum of the water RS stretching band is shifted towards low frequencies, and the downturn of the curve $\nu_{max}(C)$ is observed for solutions of CsCl. Therefore, the downturn of the curves $\nu_{max}(C)$ can be used to determine the values of the concentrations, at which point ions begin to form ion pairs in the solutions.

In this study, the width of the water Raman stretching band is characterized not by the halfwidth, but by the width at the level of 1/4 of the maximum spectrum intensity, because of the central inflection point and the asymmetric shape of the stretching band (Fig. 1). With an increasing salt concentration, the ratio of low- and high-frequency shoulders of the stretching band changes. At low concentrations, the level of the halfwidth is below the inflection point; at high concentrations, it is above the inflection point. For this reason, the dependences of the stretching band halfwidth on the concentration have peculiarities that make the comparison of these dependences for different salts incorrect. To avoid this, the width of the level at one-fourth of the maximum intensity ($\Delta\nu_{1/4}$) was chosen as the characteristic investigated: for any concentrations of the studied salts, the level of 1/4 of the maximum intensity lies below the inflection point. Hereinafter, we shall call the value $\Delta\nu_{1/4}$ "the width."

In Fig. 3, the dependences of the width of the water RS stretching band on the concentration of the halides of metals $\Delta\nu_{1/4}(C)$ are presented. With an increasing
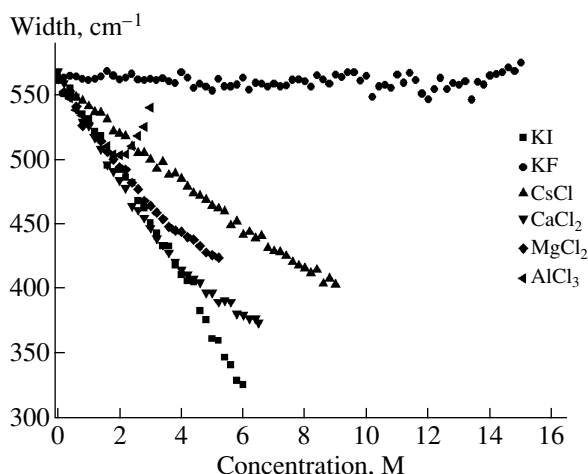
Width, cm^{-1}

Fig. 3. Dependences of the width of the Raman scattering stretching band of water in solutions on the concentration of salts $\Delta\nu_{1/4}(C)$.

salt concentration, the width $\Delta\nu_{1/4}$ decreases faster in the following row of anions: F$^-$ < Cl$^-$ < Br$^-$ < I$^-$. Negatively hydrated I$^-$, Br$^-$, and Cl$^-$ anions increase the mobility of the nearest water molecules in comparison with pure water; thus, the hydrogen bounds among water molecules weaken or break down; the molecules become less bound; and the band becomes narrower. The greater the negative hydratedness of the anion (or the surface charge density) is, the faster the decrease in the width of the water-stretching band. The experimental data obtained showed that the cations of alkali metals are close in terms of their effect on the width $\Delta\nu_{1/4}$ of the water RS stretching band. The width $\Delta\nu_{1/4}(C)$ of the RS stretching band of water in the solutions of fluorides is changeless, because the F$^-$ anion is positively hydrated.

2.1.2. Chlorides of metals. To compare the revelation of the hydration properties of the cations of uni-, bi-, and trivalent metals in water RS, the water solutions of the chlorides of Li, Na, K, Cs, Ca, Mg, Mn, Zn, and Al were investigated. Analysis of the dependences $\nu_{max}(C)$ for the RS stretching bands of water in the

MgCl$_2$, MnCl$_2$, CaCl$_2$, and BaCl$_2$ (Fig. 2) solutions showed that, unlike the solutions of the chlorides of univalent metals, the following effects are observed:

(1) The value of the shift of the water Raman stretching band maximum with an increasing concentration depends on the type of cations (Table 2) and it is changed according to the row: Ba^{2+} > Ca^{2+} > Mn^{2+} > Mg^{2+}. The obtained row is consistent with the properties of the hydration of ions. All of the cations of the salts studied are positively hydrated [11]. Ba^{2+} and Ca^{2+} cations have a smaller surface density of the charge, such that they fix the neighboring water molecules more weakly. This fact manifests itself in the greater shift of the water RS stretching band maximum compared to that for Mn^{2+} and Mg^{2+} cations, which have a greater surface density of the charge.

(2) For the solutions of the chlorides of bivalent metals, the plateau of the curves $\nu_{max}(C)$ begins at smaller values of C_{pl} (Table 2), and the maximal shifts of the water RS stretching band are also smaller. Such a result is explained by the greater ability of the cations of bivalent metals to fix water molecules, as well as the negative hydratedness of the two chloride anions, which make water molecules more bound; therefore, the shift of the Raman stretching band is smaller compared to this provided by the joint ability of the cations of univalent metals and one anion of chlorine in the solutions of alkali metals.

(3) All of the curves $\nu_{max}(C)$ for the solutions of bivalent metals have downturns (Fig. 2). According to our calculations of the Bjerrum parameter [12] in water solutions of the halides of bivalent metals, ion pairs are formed at a salt concentration of 4 M. This value agrees within a satisfactory error with the values of the concentrations C_{ip}, which were obtained in our experiments (Table 2).

Therefore, from the Raman stretching band of water in the solutions of the halides of metals, one can determine the concentrations C_{pl} and C_{ip} (Table 2), at which the short-range hydration establishes in the solution and ions begin to form ion pairs in solutions, respectively.

Table 2. Values of the shift of the maximum of the water Raman scattering valence band towards high frequencies with an increasing concentration in the solutions of the chlorides of bivalent and trivalent metals

Salt	Range of concentrations studied	Maximum shift observed at concentrations:					C_{pl}	C_{ip}
		1 M	1.6 M	3 M	5 M	maximal shift		
MgCl$_2$	0…5 M	11 cm^{-1}	13 cm^{-1}	16 cm^{-1}	7 cm^{-1}	16 cm^{-1}	1.8 M	3.8 M
MnCl$_2$	0…5.8 M	13 cm^{-1}	15 cm^{-1}	17 cm^{-1}	12 cm^{-1}	18 cm^{-1}	1.8 M	4.0 M
CaCl$_2$	0…6.4 M	15 cm^{-1}	22 cm^{-1}	31 cm^{-1}	32 cm^{-1}	33 cm^{-1}	2.2 M	5.8 M
BaCl$_2$	0…1.5 M	21 cm^{-1}	27 cm^{-1}	–	–	27 cm^{-1}	–	–
AlCl$_3$	0…3 M	8 cm^{-1}	13 cm^{-1}	−1 cm^{-1}	–	13 cm^{-1}	1.4 M	1.8 M

For water solutions of AlCl$_3$, the dependence ν_{max}(C) first increases (Fig. 2), and it begins to turn down at the concentration 1.8 M. The frequency of the maximum increases due to the total interaction of one Al^{3+} cation and three Cl$^-$ anions with water molecules. The curve ν_{max}(C) turns down due to the formation of ion pairs and associates. Additionally, for water solutions of AlCl$_3$, it was observed that, from the concentration of 0.8 M and up, an acclivous band appears in the low-frequency region of the water RS stretching band (Fig. 1). Perhaps, this band is due to the presence of strongly bound associates in the solution.

In Fig. 3, the dependences $\Delta\nu_{1/4}$(C) for the solutions of potassium and magnesium chlorides are presented. The curve $\Delta\nu_{1/4}$(C) for the solutions of the chlorides of bivalent metals, unlike the solutions of the chlorides of univalent metals, depends on the cations: the width of the water Raman stretching band decreases more quickly with an increasing concentration in the row Ba^{2+} > Ca^{2+} > Mg^{2+} > Mn^{2+}. While the dependences $\Delta\nu_{1/4}$(C) for the solutions of the chlorides of alkali metals can be fitted by a straight line, for the chlorides of bivalent metals, the dependences $\Delta\nu_{1/4}$(C) are nonlinear. Such behavior of the dependences $\Delta\nu_{1/4}$(C) is due to the total interaction of one cation of bivalent metal and two Cl$^-$ anions with water molecules. As a result of this total interaction, a weakening or break in the hydrogen bounds is less intense compared to the case of the chlorides of alkali metals, so that the width of the water RS stretching band $\Delta\nu_{1/4}$ decreases with an increasing salt concentration, although not as quickly. Therefore, the dependence $\Delta\nu_{1/4}$(C) for the solutions of the chlorides of bivalent metals is nonlinear.

The width $\Delta\nu_{1/4}$ for solutions of AlCl$_3$ (Fig. 3) is almost constant at concentrations changing from 0 to 2 M, and, then, it increases sharply. Apparently, such an increase is provided by the acclivous band appearing in the region of 3000 cm^{-1} (Fig. 1).

2.1.3. Sulphates of metals. All of the anions explored before were negatively hydrated. To study the influence of salts with positively hydrated anions on the water RS stretching band, solutions of the sulphates of the metals Li, Na, K, Cs, Mg, Mn, Zn, Fe, and Al were studied. The obtained experimental data showed that when the concentration changed within the same limits, the shape of the Raman stretching band of water in the solutions of chlorides changed substantially greater than that in the solutions of sulphates. For the solutions of the sulphates of alkali metals, a small shift in the maximum of the water RS stretching band towards higher frequencies is observed with an increasing concentration. For the solutions of the sulphates of bi- and trivalent metals, the maximum of the water RS stretching band remains almost unshifted in the whole range of the solubility of salts (Fig. 2). The width $\Delta\nu_{1/4}$ of the RS stretching band of water in the solutions of sulphates decreases by a negligible margin with an increasing concentration for the sulphates of alkali metals, and is almost constant for the sulphates of bivalent metals. For the solutions of Al$_2$(SO$_4$)$_3$, the width $\Delta\nu_{1/4}$ is almost constant when the concentration is changed from 0 to 0.5 M, increasing sharply at higher concentrations. Perhaps, this increase is generated by the presence of associates in the solution.

The weak influence of the sulphates on the water RS stretching band is explained by the following: While negatively hydrated anions Cl$^-$ increase the mobility of water molecules in hydration shells, positively hydrated sulphate-anions SO$_4^{2-}$ fix water molecules compared with pure water. However, in the solutions of sulphates, the formation of negatively hydrated anions HSO$_4^-$ is possible due to proton migration. Therefore, changes in the position and shape of the water RS stretching band depend on the total interaction of the cations of metals and SO$_4^{2-}$ and HSO$_4^-$ anions with water molecules.

Thus, in the solutions of salts with positively hydrated cations and anions, it is impossible to determine the hydration parameters from the dependences of the water RS stretching band characteristics on the salt concentration and salt type.

In this study, the revelation of the hydration properties of ions in other RS spectral bands (the bending and low-frequency bands) was investigated in the solutions of LiCl, NaCl, KCl, NaBr, KBr, and KI.

2.2. Revelation of the Hydration of Ions in the Raman Scattering Bending Band

It was observed that the frequency of the maximum of the water RS bending band in the pointed solutions is equal to 1654–1656 cm^{-1} and it does not depend on the salt type or the salt concentration in the solution in the whole range of explored concentrations.

The obtained results show that the cations and anions bring no significant influence on the bending vibrations of water molecules. Therefore, differences in the hydration properties of cations and anions are not revealed in the behavior of the water Raman bending band in any way; so, this band cannot be used to indicate the processes and parameters of hydration in solutions.

2.3. Revelation of the Hydration of Ions in the Raman Scattering Low-Frequency Bands

To distinguish the Raman scattering signal of water from the scattering at a nonshifted frequency, the R(ν) representation [13, 14] was used in this study. As a result, the water Raman low-frequency bands for the solutions of the halides of alkali metals were successfully obtained (Fig. 4). As one can see from Fig. 4, the water Raman low-frequency region has two maximums
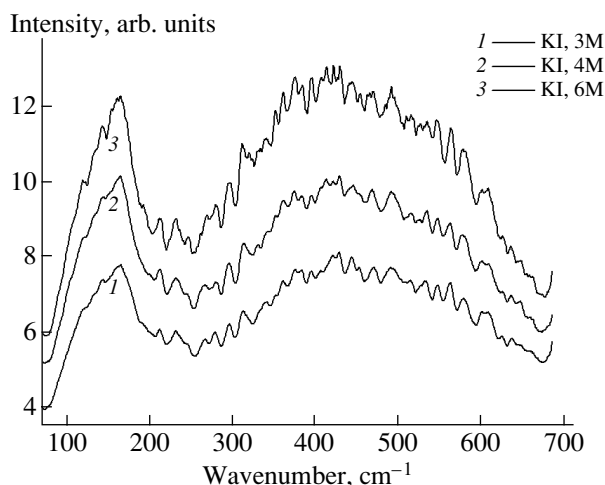
Intensity, arb. units

1 —— KI, 3M
2 —— KI, 4M
3 —— KI, 6M

Fig. 4. Low-frequency bands of the Raman scattering of water in solutions of KI at different concentrations.

at frequencies of about 70 cm^{-1} and about 186 cm^{-1}. In this study, the dependence of the shape of the Raman band with a maximum frequency 186 cm^{-1} on the type and concentration of dissolved salts was investigated. It was observed that, in the presence of the pointed salts, the maximum of this band shifts towards low frequencies (rather than towards high frequencies, as for the RS stretching band). Unlike the water RS stretching band, the shift of maximum of the water RS low-frequency band depends both on the cations and anions. For cations, this influence increases in the row $Li^+ < Na^+ < K^+$, for anions, it increases in the row $Cl^- < Br^- < I^-$. Negatively hydrated ion increases the mobility of water molecules around itself; therefore, hydrogen bounds break

Table 3. Total hydration numbers of ions in water solutions

Salt	C_{pl}	Total hydration numbers of salts	Literature data [15]
LiI	3.4 M	16	12…17
LiBr	5.2 M	11	7…15
LiCl	5.0 M	11	4…20
NaI	3.2 M	19	13…17
NaBr	3.4 M	16	8…16
NaCl	3.6 M	15	5…51
KI	2.6 M	21	15…17
KBr	3.2 M	17	10…16
CsI	2.2 M	25	15…17
CsCl	2.8 M	20	7…21
MgCl$_2$	1.8 M	31	3…32
MnCl$_2$	1.8 M	31	8…32
CaCl$_2$	2.2 M	25	8…32
AlCl$_2$	1.4 M	40	9…45

or become weak, and oxygen atoms of neighboring water molecules interact more strongly. Hence, the maximum of the RS low-frequency band (186 cm^{-1}), which is generated by the vibrations of oxygen atoms of neighboring water molecules relative to each other [5, 6, 14], shifts towards low frequencies. Surrounded by cations with a smaller surface charge density, for example, Li$^+$ and Na$^+$, the weakening of and break down of hydrogen bounds become smaller, and the change in intermolecular interactions decreases, such that the water RS low-frequency band shift towards low frequencies becomes smaller.

According to our results, the shift of the explored water RS band towards low frequencies caused by anions is smaller than that caused by cations. This is due to the ability of all of the anions studied to form hydrogen bounds with water molecules. Therefore, the break down and weakening of hydrogen bounds of water molecules surrounding anions is less intense than for water molecules surrounding cations. As a result, the influence of cations on the water RS low-frequency band with a maximum at 186 cm^{-1} is greater than the influence of anions.

Thus, the water RS low-frequency band with a maximum at 186 cm^{-1} can also be an indicator of the hydration of ions. However, the use of the low-frequency band of the water Raman spectrum for this purpose is not very convenient: first, the intensity of this band is much less than that of the water RS stretching band; second, the extraction of a useful Raman signal from a scattering signal in the low-frequency region close to the excitation line is as yet not a simple task.

2.4. Determination of the Hydration Numbers of Ions

Supposing that, at the concentration C_{pl}, all of the water molecules are distributed over the shells of short-range hydration, it is possible to determine the total hydration numbers of the studied salts. The obtained values of the concentrations C_{pl} and the total hydration numbers for the halides of uni-, bi- and trivalent metals are presented in Table 3. It is worth noting that the values of the hydration numbers reported in the literature (for example, [14]) are obtained using different methods and differ from each other by several fold. It is still difficult to determine the hydration numbers of ions with good accuracy. Satisfactory agreement of the values of the hydration numbers of salts obtained in this study with data from the literature serves as confirmation of the validity of our explanation of the behavior of the RS stretching band of water in solutions of inorganic salts.

CONCLUSIONS

As a result of research on the influence of the halides and sulphates of metals on the water RS stretching

band, it was observed that the halides of alkali metals bring the most influence on the position and shape of the water Raman stretching band in comparison with chlorides and sulphates of bi- and trivalent metals. The change of the characteristics of the water RS stretching band caused by sulphates is inconsiderable. It was observed that anions change the characteristics of the water RS stretching band much more strongly than cations. The rows for the degree of influence of anions on the Raman stretching band were confirmed, and the laws for the influence of cations on this band were established. In the presence of the salts studied in water, the position of the maximum of the water Raman bending band does not change in the whole range of solubility of salts. In this study, it was obtained that both cations and anions of the salts studied bring the influence on the Raman low-frequency band with a maximum at 186 cm^{-1}. However, cations change the characteristics of the low-frequency band much more strongly than anions. The rows for the degree of influence of cations and anions on the water Raman low-frequency band were established.

The observed laws are explained using hydration theory, and they can be used for the indication of the hydration and the determination of the hydration parameters.

The obtained results can be used to elaborate upon methods of express monitoring of levels of pollution in natural waters; in this case, they can be used to monitor levels of pollution by domestic and trade wastes including inorganic salts.

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