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Raman Spectroscopic Study of Concentrated Aqueous LiBr Solutions

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The Raman spectra for concentrated aqueous LiBr solutions $(LiBr)_x(H_2O)_{1-x}$ and $(LiBr)_x(D_2O)_{1-x}$, $x=0.05—0.25$, were measured in the frequency range of 30—1000 cm^{-1}. A polarized peak intensity centered at 160—190 cm^{-1} in the isotropic spectrum for H_2O solutions exhibits a systematic increase with increasing LiBr content. At LiBr concentrations below 15 mol%, this peak contains several shoulders at both the lower and higher frequency sides. The corresponding peak in the isotropic spectrum for D_2O solutions is shifted to the lower frequency by ca. 10 cm^{-1}. The isotropic spectra for highly concentrated H_2O solutions, such as 20 and 25 mol% LiBr, have another component at 340 cm^{-1}, which is also shifted to the lower frequency by ca. 20 cm^{-1} in D_2O solutions. This 340 cm^{-1} peak in a 25 mol% LiBr solution is also shifted to the higher frequency by ca. 13 cm^{-1} when isotopically substituting ^{6}Li (95.5% ^{6}Li) for ^{nat}Li (92.5% ^{7}Li), while the position of 190 cm^{-1} peak remains unchanged when substituting. Consequently, the peaks centered at 160—190 cm^{-1} and at 340 cm^{-1} can, respectively, be assigned to the totally symmetric stretching vibration of tetrahedrally hydrated lithium ion, $Li^+(H_2O)_4$, and that of the solvent-shared ion pair, $Li^+(H_2O)_4\cdots Br^-$, by taking into consideration the results of diffraction studies reported previously.

Aqueous solutions of lithium halogenide, LiX, have often been employed with the object of examining the hydrated-ion structure in the solution through diffraction and spectroscopic measurements due to the high solubility of LiX in water and the transparency to visible light. The hydration structure of Li^+ in aqueous solution has been investigated by X-ray diffraction,[1—8] neutron diffraction,[9—17] and molecular dynamics (MD) simulation[6—8] techniques. These results have pointed out that Li^+ has a stable first hydration shell consisting of 4—6 water molecules bonding to Li^+ with an interatomic distance of $r(Li^+\cdots O)=1.94—1.99$ Å.[9—17] This interatomic distance is almost independent on the kind of counter-ions and the solute concentration. The formation of a stable hydration structure of Li^+ has also been confirmed by recent NMR information that the spin-lattice relaxation times (T_1 and T_2) for ^{7}Li and H nuclei are strongly influenced by the librational motion of hydrated Li^+.[18] Thus, low-frequency bands related to the $Li^+\cdots O$ stretching mode in the hydrated ion, $Li(H_2O)_n{}^+$, are expected to be detected in the vibrational spectra. In fact, highly polarized Raman bands in the low-frequency region have been observed as the totally symmetric stretching mode (ν_1) associated with the structural unit, $Li^+(H_2O)_n$ (n=4 or 6).

Raman spectroscopic studies of aqueous solutions containing Li^+ have been made by several authors.[19—25] However, at present there are some conflicting interpretations of the ν_1 frequency of the $Li^+(H_2O)_n$ unit in solution. Michaelian and Moskovits have reported two polarized Raman bands at 190 and 400 cm^{-1} in their difference spectra between LiX (X=Cl, Br)–H_2O solutions and pure H_2O. They assigned these peaks to the totally symmetric and asymmetric stretching vibrations for the $Li(H_2O)_4{}^+$ tetrahedral unit, respectively.[24] However, their assignment seems to involve considerable uncertainties, because the position and intensity of the intermolecular $H_2O\cdots H_2O$ band located near to the symmetric vibrational component of the $Li(H_2O)_4{}^+$ unit tend to be different in solution and pure H_2O. Nash et al. have investigated the polarized Raman spectra observed in the intermolecular librational region (200—1100 cm^{-1}) using ^{6}Li/^{7}Li and H/D isotopically substituted aqueous LiCl and LiBr solutions.[23] They decomposed the parallel and perpendicular spectra into five Gaussian components. In their interpretation, the polarized 440 cm^{-1} component, observed in a 3.5 mol kg^{-1} solution, was ascribed to the totally symmetric stretching mode (ν_1) of the $Li(H_2O)_4{}^+$ unit. Another polarized 350 cm^{-1} component found in the 8.0 mol kg^{-1} solution was ascribed to the $Li^+\cdots O$ stretching vibration in the solvent-shared ion pair, $Li^+(H_2O)_4\cdots Br^-$. Kanno and Hiraishi have observed a highly-polarized Raman band near 170 cm^{-1} in a glassy solution of LiX (X=Cl, Br, and I), which is absent in the spectrum for pure water.[25] Such a less clear situation at assigning the vibrational modes related to the hydrated ion in the aqueous solution is considered to occur mainly due to a considerable overlap with the intermolecular librational mode between $H_2O\cdots H_2O$, which reflects the hydrogen-bonded solvent structure.

In this paper we describe the results concerning the isotropic Raman spectra for aqueous LiBr solutions with extended salt compositions of 5—25 mol% observed in the frequency range between 30 and 1000 cm^{-1}, in order to determine exact vibrational frequencies of hydrated Li^+. The more polarized modes, such as the totally symmetric stretching mode, tend to appear clearly, while the less polarized modes, such as the deformation and asymmetric stretching modes, disappear in the isotropic spectra. Accordingly, the isotropic Raman spectra can give reliable information on the $Li^+\cdots O$ symmetric stretching mode for hydrated Li^+

in an aqueous LiBr solution. In addition, the contribution from the intermolecular librational modes between water molecules near to 200 cm^{-1} can be neglected.[26,27] Measurements of D_2O solutions with the corresponding salt concentrations and on ^{6}Li-enriched samples of 10 and 25 mol% LiBr–H_2O solutions have also been carried out in order to clarify the relationship between the Raman spectra and the structure of hydrated Li^+. Moreover, the isotropic Raman spectra for 10 and 25 mol% LiCl–H_2O and –D_2O solutions and those at various temperatures for the 25 mol% LiBr–D_2O solution have been measured in order to investigate the influence of halogen substitution and the destruction of the hydrogen-bonded structure on the respective Raman components.

Experimental and Data Analysis

LiBr·H_2O and LiCl (Nacalai tesque Inc., Guaranteed grade) were both dried in vacuo at 180 °C to obtain anhydrous ^{nat}LiBr and ^{nat}LiCl (natural abundance, 92.5% ^{7}Li). ^{6}Li-enriched LiBr was prepared by reacting $^6Li_2CO_3$ (95.45% ^{6}Li Tomiyama Chemical Co., Ltd.) with slightly excess amounts of concentrated aqueous hydrobromic acid solution. Dehydration of the product solution was achieved by heating at 180 °C under vacuum for two days. The sample solution was prepared by dissolving weighted amounts of anhydrous salt in distilled water and in D_2O (99.9% D, Aldrich Chemical Inc.). The solution was filtered with a 0.45 μm teflon millipore filter before introducing it into a pyrex Raman cell (10×10 mm, 40 mm H), in order to remove dust particles. The Raman spectra were observed at 25 °C in the frequency region of 30—1000 cm^{-1} using a JASCO NR-1100 spectrometer with a 514.5 nm line of an NEC GLG-3200 Ar^+ laser operated at 200 mW. The Raman intensities were recorded at 1 cm^{-1} intervals in both the parallel and perpendicular polarization modes with a spectral slit width of 5 cm^{-1}. Each run with a scan speed of 30 cm^{-1} min^{-1} was repeated ten times for data accumulation. The Raman spectra for a 25 mol% LiBr solution were measured in an undercooled liquid state. This solution was stable for several weeks after the measurement. Measurements at t=100, 115, and 150 °C for the 25 mol% LiBr–D_2O solution were carried out using a high-temperature furnace. The calibration for the monochromator was made using 89 of neon emission lines. The efficiency of the polarization filter was checked by measuring the ν_1 frequency of the CCl_4 molecule in the liquid state. A correction of the observed spectra for the Bose–Einstein factor, needed to distinguish low-frequency components, was made according to the following equation:[27—29]

$$I^{\mathrm{corrected}}(\nu) = (\nu_0 - \nu)^{-4} \cdot \nu \cdot [1 - \exp(-h\nu)/kT] \cdot I^{\mathrm{obs}}(\nu), \tag{1}$$

where ν and ν_0 are the Stokes Raman shift and the wavenumber of the incident light, respectively. The isotropic Raman intensity ($I^{\mathrm{iso}}(\nu)$) is obtained by

$$I^{\mathrm{iso}}(\nu) = I^{\parallel}(\nu) - 4/3 \cdot I^{\perp}(\nu), \tag{2}$$

where $I^{\parallel}(\nu)$ and $I^{\perp}(\nu)$ denote the corrected parallel and perpendicular spectra, respectively. An analysis of the peaks in the isotropic spectrum was performed employing the SALS program.[30] A Gaussian band shape was assumed for each component within the band peak.

Results and Discussion

The parallel and perpendicular spectra observed for 10 and 25 mol% LiBr–H_2O solutions are shown in Fig. 1. An indication for the polarized peak at ca. 170 cm^{-1} is predominant in both solutions. This peak position is in good agreement with that of the intermolecular stretching mode associated with the hydrogen-bond interaction between neighboring water molecules in pure liquid H_2O.[26,29] However, since the $H_2O \cdots H_2O$ stretching mode in pure water has been proved to have a purely depolarized nature,[26] it appears that the 170 cm^{-1} band in LiBr solutions contains an alternative polarized component. A broad envelope located at 300—800 cm^{-1} is, in appearance, similar to the depolarized intermolecular librational band in the spectrum for pure water.[20,26] However, a careful observation shows that the scattering intensity at around 350 cm^{-1} in the parallel spectrum ($I^{\parallel}$) increases with increasing LiBr content. Particularly, an evident shoulder can be seen at ca. 350 cm^{-1} in the parallel spectrum for the 25 mol% LiBr solution. This suggests that a new polarized component is developed in concentrated LiBr solutions.

Figure 2 represents the composition dependence of isotropic spectra involving a few highly-polarized peaks in H_2O solutions. Each peak is decomposed into three or four Gaussian components. The background intensity was estimated in terms of a third-order polynomial. The intensities of the components at ca. 100 and ca. 200 cm^{-1} obviously increase with increasing LiBr con-

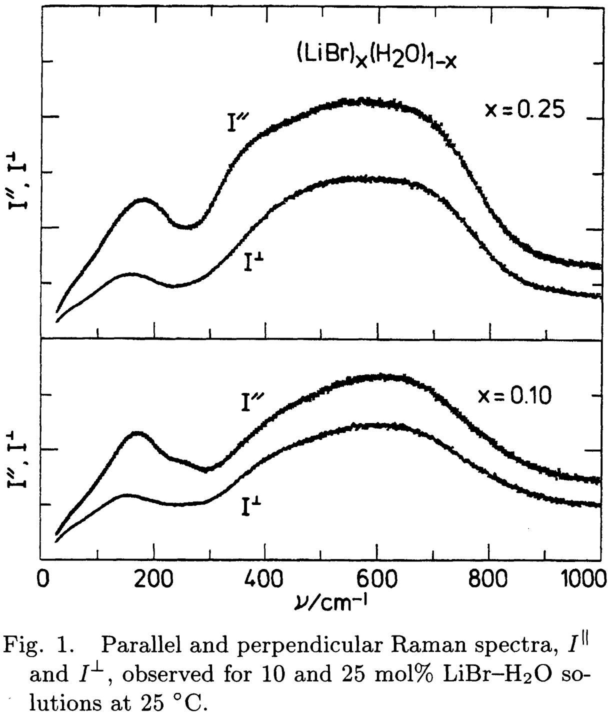

Fig. 1. Parallel and perpendicular Raman spectra, $I^{\parallel}$ and $I^{\perp}$, observed for 10 and 25 mol% LiBr–H_2O solutions at 25 °C.

Table 1. The Peak Position, Full Width at Half Maximum, and Peak Height of Gaussian Components Derived from the Least Squares Fit of the Isotropic Raman Spectra for Aqueous LiBr Solutions, v, w, and h, Respectively[a)]

		Peak A			Peak B			Peak C			Peak D			Peak E		
x	Solvent	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h
0.25	H_2O	96.7(9)	99(2)	0.536(9)	192.0(2)	107.3(1)	1.740(5)	—	—	—	344.8(2)	128.1(8)	1.485(7)	538(2)	331(5)	0.415(5)
	D_2O	101(8)	99(9)	0.50(6)	183(2)	95(4)	1.51(7)	—	—	—	323(2)	128(6)	0.84(7)	444(9)	202(14)	0.75(6)
	H_2O[b)]	97(1)	99(3)	0.52(1)	193.4(5)	110(1)	1.79(2)	—	—	—	358.4(6)	137(2)	1.59(2)	540(3)	328(7)	0.373(6)
0.20	H_2O	97(5)	93(7)	0.53(4)	194(1)	106(3)	2.32(3)	—	—	—	334(1)	110(3)	0.92(1)	—	—	—
	D_2O	90(4)	84(6)	0.50(5)	182.3(8)	101(3)	2.22(5)	—	—	—	310(2)	111(7)	0.60(4)	446(10)	232(24)	0.46(6)
0.15	H_2O	103(18)	96(19)	0.4(1)	187(3)	93(11)	1.53(9)	259(5)	59(11)	0.3(1)	329(7)	106(13)	0.30(2)	—	—	—
	D_2O	94(10)	79(12)	0.25(6)	176(1)	89(7)	1.38(3)	246(3)	56(8)	0.30(8)	312(9)	87(15)	0.16(1)	—	—	—
0.10	H_2O	97(1)	71(3)	0.318(9)	174.7(2)	79.6(6)	1.500(9)	252.6(5)	75(1)	0.694(9)	333(2)	88(4)	0.203(9)	—	—	—
	D_2O	87(7)	64(9)	0.18(4)	167(1)	86(6)	1.33(2)	244(3)	65(11)	0.49(8)	307(20)	70(24)	0.11(4)	—	—	—
	H_2O[b)]	106(2)	87(4)	0.227(9)	176.3(3)	80.7(9)	1.02(1)	252.4(7)	73(2)	0.475(9)	338(2)	90(7)	0.140(9)	—	—	—
0.05	H_2O	100(2)	71(5)	0.133(7)	164.9(5)	77(1)	0.601(7)	246.7(9)	86(2)	0.308(7)	—	—	—	—	—	—
	D_2O	105(22)	60(19)	0.1(1)	157(5)	69(12)	0.57(8)	233(6)	84(8)	0.32(2)	—	—	—	—	—	—

a) Estimated standard deviations are given in parentheses. b) ^{6}Li-enriched sample.

tent. The relative intensity of the component at ca. 250 cm^{-1}, which is observed as a shoulder at the high-frequency side of the 200 cm^{-1} peak in a 5 mol% solution, decreases with increasing LiBr content. Furthermore, a new component at ca. 350 cm^{-1} becomes predominant at higher LiBr concentrations above 10 mol%. An additional broad component centered around 500 cm^{-1} appears in the spectrum for the 25 mol% LiBr solution. These components, except for the 500 cm^{-1} one, are considered to be caused by the intermolecular $Li^+\cdots OH_2$ and probably $Br^-\cdots H_2O$ stretching vibrations with the higher symmetry. The peak parameters for these components (termed A, B, C, D, and E) are listed in Table 1.

The isotropic spectra for D_2O solutions with the corresponding LiBr concentrations are given in Fig. 3. The Gaussian components (A, B, C, and D) identified in H_2O solutions, are also apparent in these D_2O solutions. A newly developed broad band located at ca. 450 cm^{-1} is observed in 20 and 25 mol% LiBr solutions. The peak parameters for the Gaussian components (A, B, C, D, and E) for D_2O solutions, which are analyzed in the same manner applied to H_2O solutions, are summarized in Table 1. Assuming that the symmetric stretching mode in hydrated Li^+, $Li(H_2O)_n{}^+$ or $Li(D_2O)_n{}^+$ is involved in these components, the ratio of the vibrational frequency of this mode for the D_2O solution to that for the H_2O solution is approximately calculated as follows,[24)] considering tetrahedral ($n=4$) or octahedral ($n=6$) geometries around Li^+:

$$\nu_{\mathrm{D_2O\ soln}}/\nu_{\mathrm{H_2O\ soln}} \sim (m_{\mathrm{H_2O}}/m_{\mathrm{D_2O}})^{1/2} = 0.95. \tag{3}$$

This value corresponds well to the ratio $\nu_{\mathrm{D_2O\,soln}}/\nu_{\mathrm{H_2O\,soln}}$ for the observed peak components of B, C, and D (0.93—0.97), whereas, no systematic change in the position of peak A can be found between H_2O and D_2O solutions, suggesting that only components B, C, and D are closely related to the symmetric stretching mode in $Li(H_2O)_n{}^+$ or $Li(D_2O)_n{}^+$ structural units.

According to the neutron-diffraction result, the hydration number of Li^+ (n_{LiO}) in a 3.06 mol% LiBr heavy water solution has been reported to be 4.5±0.5 with an $Li^+\cdots O$ distance of 1.94 Å.[16)] For a 20 mol% LiBr solution, n_{LiO} and r_{LiO} have been shown to be 3.9±0.5 and 1.96 Å, respectively.[17)] These $Li^+\cdots O$ distances reported in LiBr solutions are nearly equal to the average r_{LiO} (=1.94 Å) in various crystalline hydrates, in which Li^+ is coordinated by four water molecules with T_d symmetry.[31)] In the case of highly coordinated structures, r_{LiO} has been stated to be much larger, i.e., 2.1—2.2 Å in the six-fold coordination.[31)] Therefore, the hydration number of Li^+ in 3—20 mol% LiBr solutions can be judged to be close to four. We thus assign peaks B and C in the isotropic spectrum for a 5 mol% LiBr solution to the totally symmetric stretching mode in tetrahedrally hydrated Li^+, $Li(H_2O)_4{}^+$ or $Li(D_2O)_4{}^+$. The presence of peak B in the spectrum for the 25 mol% LiBr solution also implies that considerable amounts of water molecules are simultaneously shared by different lithium ions, because there exist less than four water molecules per one Li^+ in this highly concentrated solution. In addition, the observed ratio $\nu_{\mathrm{D_2O\,soln}}/\nu_{\mathrm{H_2O\,soln}}$ for peak D, which is evident at LiBr concentrations above 20 mol%, lies at 0.93—0.94, suggesting that this peak also arises from the $Li^+\cdots OH_2$ stretching vibration. In order to clarify the origin of peak D, measurements of isotopically substituted samples, $(^6LiBr)_{0.25}(H_2O)_{0.75}$ and $(^6LiBr)_{0.10}(H_2O)_{0.90}$, were carried out, in which only the mass of the lithium ion was changed (Fig. 4).

The positions of peaks B and C for the ^{6}Li-enriched (95.5% ^{6}Li) 10 mol% LiBr solution are almost identical to those for the natural-Li (92.5% ^{7}Li) solution within the experimental errors. For the 25 mol% LiBr solution, only a small frequency shift is observed for peak B, while, peak D has a 13 cm^{-1} higher frequency shift when substituting ^{6}Li to $^{\mathrm{nat}}$Li. These results indicate that Li^+ varies only slightly in its position during the vibrational motion associated with peaks B and C, reflect-

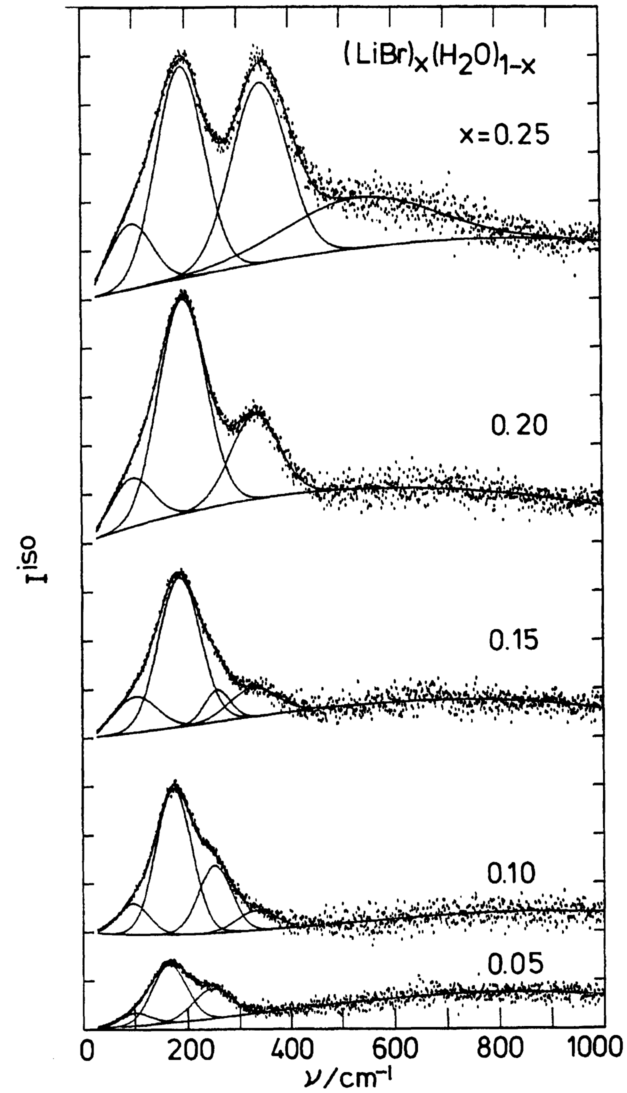

Fig. 2. Composition dependence of the isotropic Raman spectrum for aqueous LiBr–H_2O solutions, $(LiBr)_x(H_2O)_{1-x}$, at 25 °C. The Gaussian components derived from a least-squares fit are indicated by solid lines.

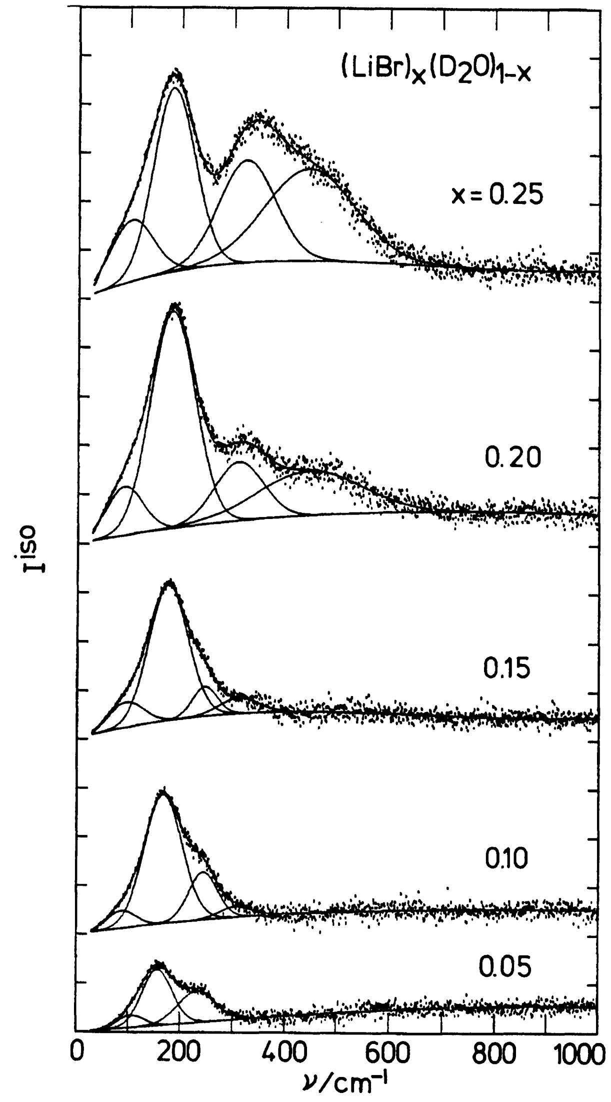

Fig. 3. Same notations as in Fig. 2, except for the heavy water solutions, $(LiBr)_x(D_2O)_{1-x}$.

ing the well-defined symmetrical stretching mode, ν_1, while, it does move in the vibrational motion associated with peak D with a loss of Td symmetry around Li^+. Then, two possible interpretations for the hydrated structure of Li^+ can be proposed from the result for peak D. One is to connect this peak with the $Li^+\cdots OH_2$ symmetric stretching mode in the $Li^+Br^-(H_2O)_3$ structural unit involving a direct contact of Li^+ and Br^-. Another interpretation is that peak D is caused by the symmetric stretching vibration of the H_2O molecule-shared ion pair, $Li^+(H_2O)_4\cdots Br^-$, in which the first coordination shell of Li^+ is fully occupied by four water molecules and one Br^- is attached to H_2O molecules in the first hydration shell of Li^+. The formation of direct or indirect ion pairs, $Li^+\cdots X^-$, in highly concentrated aqueous LiX solutions has frequently been proposed based on tracer diffusion measurements,[32] neutron diffraction[12] and MD simulations.[8] Peak D is significant in very highly concentrated solutions, such as 20 and 25 mol% LiBr, but already appears in the spectrum of 15 mol% or probably 10 mol% LiBr solutions, as can be seen in Figs. 2 and 3. It seems unlikely that the contact ion pair, $Li^+\cdots Br^-$, is formed in such low salt concentrations, even if the intermolecular hydrogen bonded structure in the solvent is somewhat destroyed. The neutron-diffraction result has also proved that no indication of a contact ion-pair has been detected in the 20 mol% LiBr solution.[17] Consequently, it may reasonably be considered to assign peak D to the $Li^+\cdots OH_2$ stretching mode in the structural unit, $Li^+(H_2O)_4\cdots Br^-$, with the solvent molecule-shared ion pair.

The origin of peak A at ca. 100 cm^{-1} observed in the present spectra is less clear. It may possibly be supposed that the symmetric stretching mode

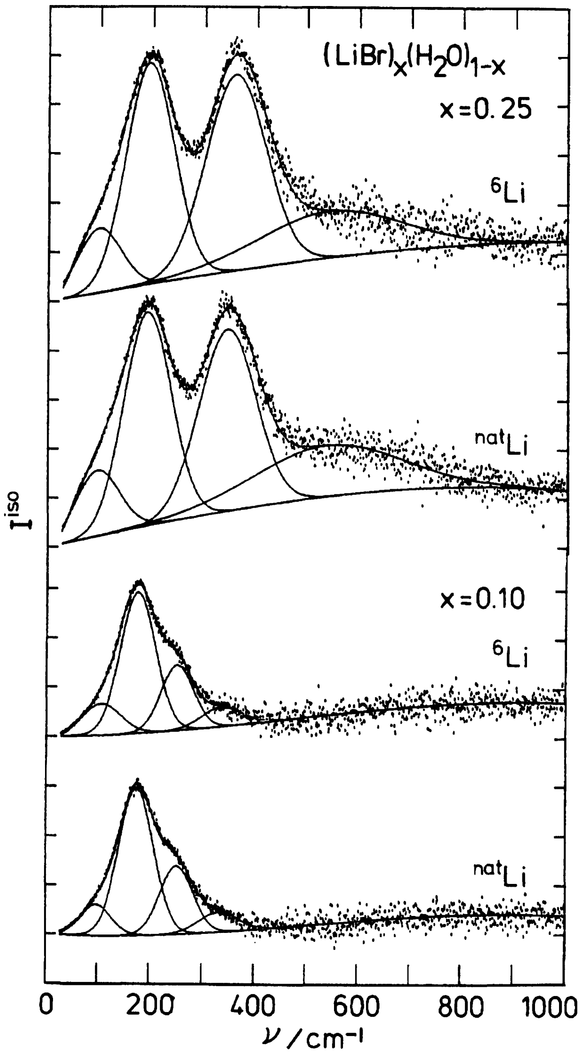

Fig. 4. Isotropic Raman spectra for 10 and 25 mol% ^{6}LiBr (^{6}Li : ^{7}Li=95.5 : 4.5) and ^{nat}LiBr (^{6}Li : ^{7}Li= 7.5 : 92.5)–H_2O solutions at 25 °C.

of the $Br^-\cdots H_2O$ bond in the hydrated bromide ion, $Br(H_2O)_6{}^-$,[5] exists in this frequency range.

Concerning a broad component (termed E), which is observed at higher LiBr concentrations above 20 mol%, we have still no exact information concerning its origin at present. This broad peak may be created through the procedure of the data-analysis. However, it is apparently involved in the Raman spectra for other concentrated aqueous solutions, such as the LiCl solution described later (Fig. 6a). Assuming that this is not an artifact peak, its origin seems to be related to the librational mode associated with a certain intermolecular hydrogen-bonded structure, because the observed large frequency shift (−94 cm^{-1}) in 25 mol% LiBr–H_2O and –D_2O solutions roughly corresponds to the difference in the librational frequency between pure liquid H_2O and D_2O.[33] It will be sufficiently accepted that the intermolecular hydrogen bonded structure in liquid water is very sensitive to any temperature variation. The breakdown of the hydrogen-bonded network structure ought to result in a remarkable change in the Raman spectra in the low-frequency region.[20,29] Thus, the temperature dependence of isotropic spectrum for the 25 mol% LiBr–D_2O solution was measured, the result of which is given in Fig. 5. The peak parameters of each Gaussian component are listed in Table 2. Unexpectedly, no clear effect of the temperature on position E is seen, except for a slight increase in the peak intensity with increasing temperature. In any case, it should be essential to obtain further experimental information for aqueous solutions involving other hydrated halide ions, in order to confirm the present interpretation for peaks A and E.

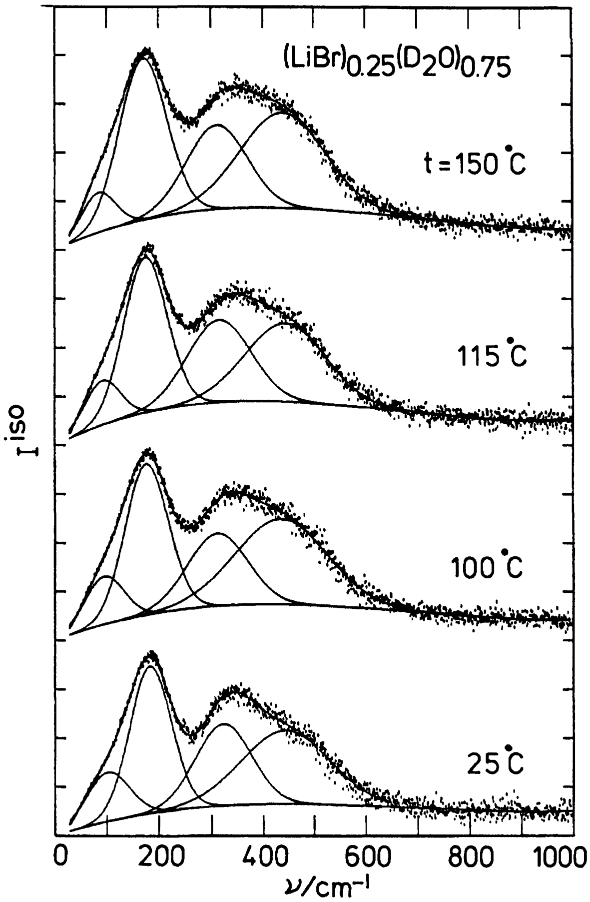

Fig. 5. Temperature dependence of the isotropic Raman spectrum for the 25 mol% LiBr–D_2O solution. The four Gaussian components are indicated by solid lines.

In Fig. 5, positions A and B indicate a small shift toward the lower frequency side and the peak intensity of D decreases upon raising the temperature. Nevertheless, it may possibly be stated by the overall result in Fig. 5 that the first hydration shell of Li^+ in the 25 mol% LiBr solution is considerably stable, even at high temperatures, such as 150 °C. An extremely low vapor pressure of highly concentrated LiBr solutions supports the formation of stable local order around Li^+, i.e., $Li^+\cdots OH_2\cdots Br^-$ solvent molecule-shared ion pair,

Table 2. The Peak Parameters of Gaussian Components for 25 mol% ^{nat}LiBr–D_2O Solution at 25—150 °C$^{a)}$

	Peak A			Peak B			Peak D			Peak E		
t/°C	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h
150	84(4)	78(5)	0.41(5)	170(1)	108(4)	1.65(4)	312(3)	137(9)	0.86(8)	439(7)	194(10)	0.98(6)
115	92(4)	82(5)	0.45(5)	175(1)	99(4)	1.59(4)	316(5)	143(10)	0.84(8)	444(9)	183(12)	0.80(7)
100	94(6)	90(7)	0.49(6)	177(2)	98(4)	1.54(6)	312(3)	136(9)	0.74(9)	436(9)	209(13)	0.88(6)
25	101(8)	99(9)	0.50(6)	183(2)	95(4)	1.51(7)	323(2)	128(6)	0.84(7)	444(9)	202(14)	0.75(6)

a) Estimated standard deviations are given in parentheses.

Table 3. The Peak Parameters of Gaussian Components for 10 and 25 mol% ^{nat}LiCl–H_2O Solutions$^{a)}$

		Peak A			Peak B			Peak C			Peak D			Peak E		
x	Solvent	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h	v/cm^{-1}	w/cm^{-1}	h
0.25	H_2O	108(1)	102(2)	0.590(9)	203.2(4)	105.6(8)	1.73(1)	—	—	—	369.6(6)	139(2)	1.25(2)	577(3)	370(6)	0.829(6)
	D_2O	108(1)	85(2)	0.339(7)	196.3(3)	93.0(9)	1.26(1)	—	—	—	345(10)	131(2)	0.458(6)	436(1)	243(4)	0.56(1)
0.10	H_2O	102(3)	75(7)	0.114(9)	191(2)	95(4)	0.76(1)	259(2)	60(7)	0.28(5)	345(10)	147(19)	0.157(8)	—	—	—
	D_2O	111(3)	57(8)	0.066(8)	182(2)	81(3)	0.559(9)	244(2)	50(3)	0.27(2)	321(6)	108(14)	0.049(6)	—	—	—

a) Estimated standard deviations are given in parentheses.

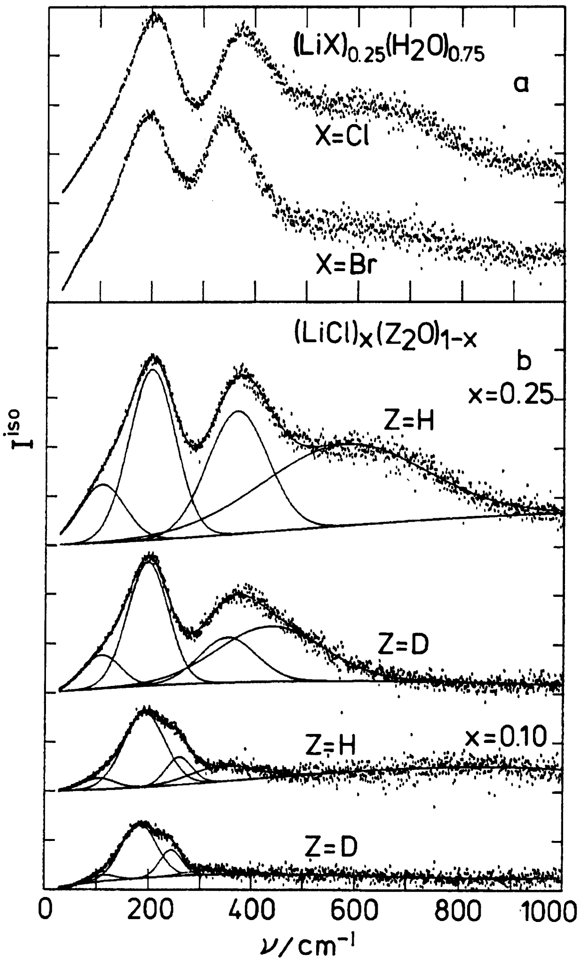

Fig. 6. a) Comparison of the isotropic Raman spectrum between 25 mol% LiCl and LiBr–H_2O solutions. b) Isotropic Raman spectra for 10 and 25 mol% LiCl–H_2O and –D_2O solutions at 25 °C.

which may prevent the vaporization of water molecules in the solution.

In order to make sure of the peak assignment of the Raman spectrum in LiBr solutions hitherto discussed, isotropic Raman spectra for 10 and 25 mol% ^{nat}LiCl–H_2O and –D_2O solutions were measured and analyzed in the same manner applied to LiBr solutions. In Fig. 6a, the observed isotropic spectrum for the 25 mol% LiCl–H_2O solution is compared with that for the LiBr–H_2O solution with the same salt concentration. A similar appearance of these spectra may reflect a strong resemblance in the intermolecular short-range structure between both solutions. The position of the band component at ca. 200 cm^{-1} shifts only a little upon replacing the halide ion, suggesting that component B arises from the vibrational mode in the common chemical species in both solutions, that is, hydrated lithium ion, $Li^+(H_2O)_n$. On the contrary, a significant difference can be observed in the vibrational frequency of the component at ca. 350 cm^{-1} between LiCl and LiBr solutions. Therefore, component D is obviously related to the vibrational mode, depending on the kind of anions. Figure 6b represents the Gaussian decomposition of isotropic Raman spectra in 10 and 25 mol% LiCl–H_2O and –D_2O solutions. The peak parameters for each component are listed in Table 3. The $\nu_{D_2O\,soln}/\nu_{H_2O\,soln}$ ratio for the observed peak components of B, C, and D (0.93—0.97) evidences that these components can be assigned to the $Li^+\cdots OH_2$ symmetric stretching mode in $Li^+(H_2O)_n$ (peaks B and C) and $Li^+(H_2O)_n\cdots Cl^-$ (peak D).

In summary, totally symmetric stretching frequencies for both tetrahedrally hydrated lithium ion, $Li^+(H_2O)_4$, and solvent-shared ion pair, $Li^+(H_2O)_4\cdots Br^-$, in aqueous LiBr solutions have been identified from the present isotropic Raman spectra such as 192 and 345 cm^{-1}, respectively, for the 25 mol% LiBr–H_2O solution. It is very worthwhile to offer structural information concerning the first hydration shell of Li^+ in highly concentrated LiBr solutions as well as the intermolecular hydrogen-bonded structure of the solvent. Along this line, neutron-diffraction experiments for the 25 mol% LiBr solution with $^6Li/^7Li$ and H/D isotopic substitution techniques are in hand to determine the partial distribution functions in solution.

All of the calculations in the present work were carried out with the ACOS 3600 computer at the Computing Center of Yamagata University.

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