Raman Spectroscopic Study on the Temperature Dependence of the Uncoupled O–D Stretching Band from HDO Molecules in Concentrated Aqueous $Zn(ClO_4)_2$ Solutions

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Polarized Raman spectra of the uncoupled O–D stretching vibrational bands in concentrated aqueous $Zn(ClO_4)_2$ solutions have been recorded in the temperature range of 26—95 °C. Observed isotropic and anisotropic spectra have been analyzed by a double-difference method, in conjunction with a least squares fitting procedure, to deduce Raman band components arisen by HDO molecules in the first hydration shell of the constituent ions in the solution. Two band components centered near 2420 and 2640 cm^{-1} were assigned to the O–D stretching vibrational mode of HDO molecules coordinated to Zn^{2+} and ClO_4^-, respectively. These frequencies agree with the infrared double-difference results. Further, it has been found that the relative integrated intensity of the ion-perturbed O–D bands is quite different from that of the 'bulk' HDO molecules. The temperature dependence of peak parameters such as the frequency and peak area for Zn^{2+} and ClO_4^--perturbed bands is very small in the temperature range of 26—95 °C, in contrast to a pronounced collapse of the band from bulk HDO molecules at elevated temperatures. This suggests that the local structure around these ions in the solution changes little in the temperature range examined in this study.

Vibrational spectroscopy is one of the most useful experimental methods to investigate how the hydrogen-bonded liquid structure varies by the coexistence of solute ions. A large number of Raman[1,2] and infrared[3] studies have been done, focusing upon the elucidation of the intramolecular O–H vibrational mode of water molecules in aqueous solutions. However, despite a lot of efforts to deduce detailed information of this mode component from observed spectra, an unambiguous interpretation for the intramolecular O–H vibrational mode has not yet been established for the following reasons. First, the coupling effect of intra- and inter-molecular vibrational modes makes the deduction of the O–H stretching band too difficult.[4] Secondly, the intramolecular O–H stretching band is composed of several band components arising from water molecules in different hydrogen-bonding states, which strongly overlap each other in the spectrum. As an attempt to avoid these difficulties, Raman spectroscopic studies of the uncoupled O–D stretching band of HDO molecules have hitherto been made, e. g., measurement of the Raman spectrum for dilute solutions of D_2O in H_2O.[5—14] The observation of such uncoupled O–D stretching bands has the advantage that the data analysis of spectra becomes much simplified because of the disappearance of intra- and inter-molecular coupling effects. The following results of the uncoupled O–D stretching band have been reported through a series of Raman spectrum studies by Walrafen.[6—8] 1) The uncoupled O–D stretching band centered near 2500 cm^{-1} has an asymmetric shape accompanied with a higher frequency shoulder at about 2650 cm^{-1}. 2) The intensity of this shoulder increases with increasing temperature. 3) The shoulder appears as a well-resolved peak in solutions containing 'structure breaking anions' such as PF_6^-, BF_4^-, and ClO_4^-. He has classified these band components involved in the total uncoupled O–D stretching band into contributions from hydrogen-bonded water molecules (ca. 2500 cm^{-1}) and from non-hydrogen bonded ones (ca. 2650 cm^{-1}), referring to the two-state model of liquid water.

Quantitative information on the uncoupled O–D oscillator located in the first coordination shell of constituent ions in aqueous solution has been obtained by double-difference analysis for infrared absorption spectra. The information can be summarized as follows.[15—23] 1) The observed O–D stretching band is separated into three contributions from HDO molecules neighboring the cation (a) and anion (b), and from the other bulk HDO molecules (c). 2) The band shape of these contributions cannot be represented by a single symmetrical Gaussian function. 3) The O–D stretching vibrational mode has a characteristic frequency and band width depending on the kind of neighboring ions. 4) There is a simple correlation between the O–D vibrational mode frequency and intermolecular distance of the ion and hydrating HDO molecules.

It is expected that a similar double-difference analysis for polarized Raman spectra in aqueous solutions gives not only a quantitative interpretation for the O–D stretching vibrational mode, but also new information on the polarizability of HDO molecules in different hydrogen-bonding states. Moreover, knowledge on the symmetry of the electron cloud within these HDO molecules can also be provided.

In this paper we describe the results of the polarized Raman spectra for both 2 and 4 mol% $Zn(ClO_4)_2$ aqueous solutions. The double-difference analysis was applied to the observed data to deduce the O–D stretching band components from HDO molecules coordinated to Zn^{2+} and ClO_4^-, respectively. The temperature dependence of these band components is also investigated to analyze the effects of temperature variation on the ion–water molecules interaction in aqueous solution.

Experimental and Data Analysis

An aqueous solution of zinc(II) perchlorate (2 and 4 mol%) was prepared by dissolving the required amounts of $Zn(ClO_4)_2\cdot 6H_2O$ (Mitsuwa Pure Chemicals, Guaranteed grade) into distilled water or a H_2O–D_2O mixture (D_2O: Merck 99.75% D). Ten mol% D_2O in H_2O was chosen as the isotopic composition of hydrogen in dilute HDO solutions considering that the intermolecular coupling effect is negligibly small[9] and that sufficient statistical accuracy of the difference spectrum is established. The sample solution was filtered with a 0.45-μm Teflon® millipore filter to remove dust particles, before introducing it into a pyrex Raman cell (10×10 mm, 40 mm H). Raman spectra were observed at 26 °C in the frequency region 2000—3000 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. Raman intensities were recorded at 1 cm^{-1} intervals in both 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 20 times for data accumulation. Measurements at 50, 75, and 95 °C were also done using a high temperature furnace. The measurement of the ν_1 band of ClO_4^- was done in the frequency region 800—1100 cm^{-1} for the purpose of internal intensity calibration between H_2O and HDO solutions.[24] The calibration of the monochromator was made using 89 of the neon emission lines. The efficiency of the polarization filter was checked by measuring the ν_1 frequency of CCl_4 in the liquid state.

The correction for the Bose–Einstein factor in the observed spectrum was made according to the following equation:[25—27]

$$I^{\text{corrected}}(\nu) = (\nu_0 - \nu)^{-4}\cdot\nu\cdot[1 - \exp(-h\nu/kT)]\cdot I^{\text{obsd}}(\nu), \quad (1)$$

where ν and ν_0 are the Stokes Raman shift and wavenumber of the incident light, respectively. Iso- and anisotropic Raman intensities are given by

$$I^{\text{iso}}(\nu) = I^{//}(\nu) - 4/3\cdot I^{\perp}(\nu)$$

and

$$I^{\text{aniso}}(\nu) = 4/3\cdot I^{\perp}(\nu), \quad (2)$$

where, $I^{//}(\nu)$ and $I^{\perp}(\nu)$ denote corrected parallel and perpendicular spectra, respectively.

The double-difference method, which has been used to observed infrared absorption spectra by Kristiansson et al.,[15—23] can remove spectral contributions from pure H_2O and from HDO molecules in the bulk state, and deduce O–D stretching band components from ion-perturbed HDO molecules. Basic assumptions in the application of the method are: 1) One-half of the contribution from HDO molecules coordinated to the anion is included in the bulk contribution, because only O–D bonds facing the anion in these HDO molecules can contribute to the anion-perturbed band. 2) The band shape of the bulk molecule component can be approximated by the uncoupled O–D stretching band in pure water. The validity of these assumptions in the double-difference method has been verified in infrared spectrum studies for various solutions.[15—23] Thus, this method is used on this Raman scattering data.

Figure 1 shows the outline of the double-difference analysis in this observed Raman spectra. The following four spectra were used to obtain the uncoupled O–D stretching band from HDO molecules in the first hydration shell of the ion, (A) 4 mol% $Zn(ClO_4)_2$ in 10 mol% D_2O–H_2O, (B) 4 mol% $Zn(ClO_4)_2$ in H_2O, (C) 10 mol% D_2O–H_2O and (D) pure H_2O, respectively. To remove the contribution from the strong O–H stretching band centered at ca. 3300 cm^{-1} in Figs. 1a and 1b, differences (A) − (B) and (C) − (D) were taken (Figs. 1c and 1d, respectively). Since it seems very difficult to find the absolute peak intensity in Raman spectrum measurements, the intensity standard should be set up to normalize the scattering intensity from different data sets. A subtraction coefficient, k_1, between two $Zn(ClO_4)_2$ solutions, (A) − (B), is obtained using the integrated ν_1 peak intensity of ClO_4^- under the condition that the number of O–H bonds is equal in both spectra. Another coefficient, k_2, between (C) and (D) is also set from the requirement that the integrated intensity of both spectra must be equal in the range of 2800—3000 cm^{-1}. The next step of the double-difference method is to decide on a coefficient, k_3, reflecting the contribution of bulk molecules to the total O–D stretching band. The value of k_3 is obtained using the least squares fitting procedure, in which the following residual sum of squares, $\sum\Delta^2$, is minimized,

$$\begin{aligned}\sum\Delta^2 = \sum[&\{A(\nu) - k_1\cdot B(\nu)\}\\ &-k_3\{C(\nu) - k_2\cdot D(\nu)\}\\ &-\psi_+(\nu) - \psi_-(\nu) - a\nu - b]^2,\end{aligned} \quad (3)$$

where, a and b denote two coefficients of a straight background function. $\psi_+(\nu)$ and $\psi_-(\nu)$ are peak profile functions of cation- and anion-perturbed O–D stretching bands used in the infrared double-difference study by Kristiansson et al.,[17] which can reproduce an asymmetric shape of the ion-perturbed O–D stretching band. These functions are expressed by

$$\psi_i(\nu) = h_i/\{1 + (\nu - \nu_i)^2/w_{i,j}{}^2\}^2 \quad (i = + \text{ or } -). \quad (4)$$

In Eq. 4, h_i and ν_i indicate the peak-height and position, respectively. $w_{i,j}$ is the peak width parameter. The value $w_{i,1}$ is used for $\nu < \nu_i$ and $w_{i,2}$ for $\nu > \nu_i$, respectively. The full width at half maximum-position, $fwhm_i$, and peak area, $Area_i$, are respectively calculated using values of $w_{i,j}$, as

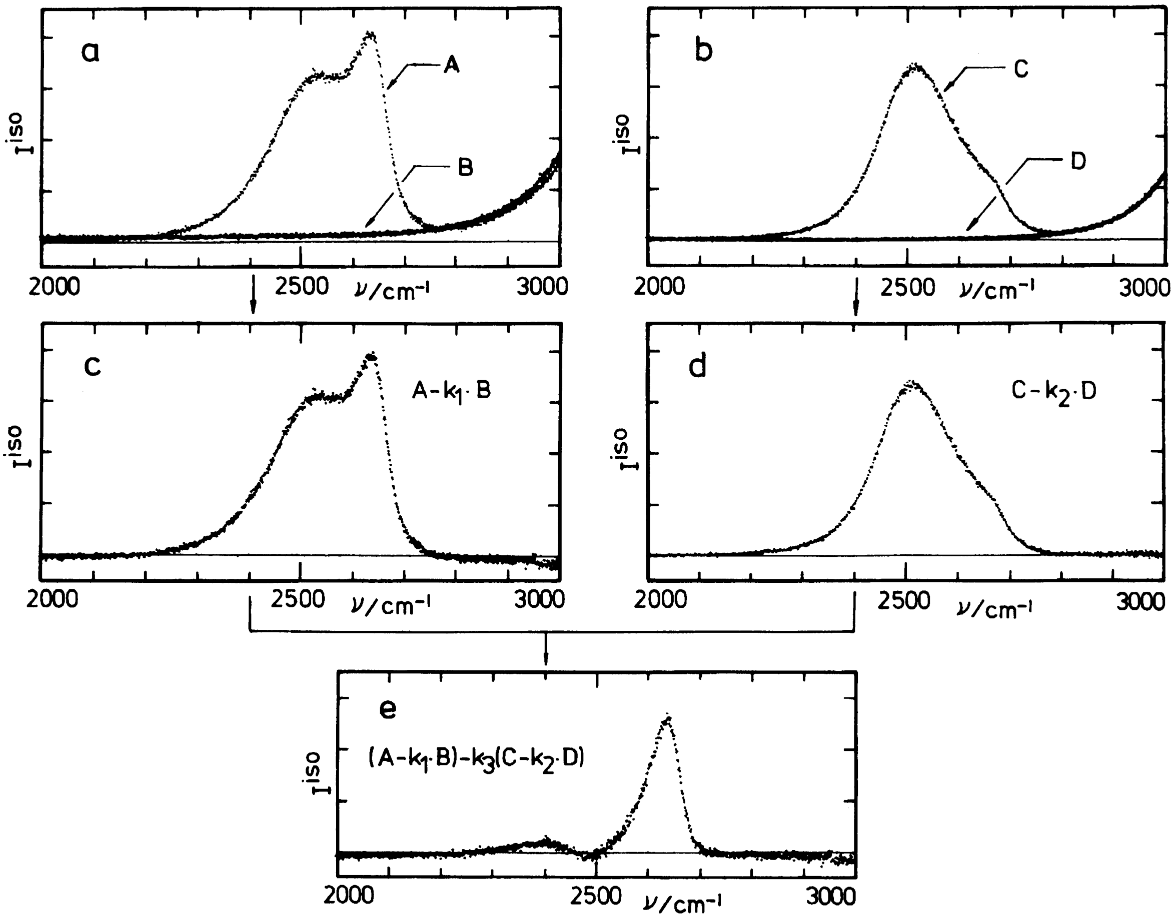

Fig. 1. The double-difference method for the isotropic Raman intensities of uncoupled O–D stretching bands. a) Observed spectra of 4 mol% Zn(ClO$_4$)$_2$ solution containing 10 mol% D$_2$O (A) and 4 mol% Zn(ClO$_4$)$_2$ solution (B). b) Observed spectra of water containing 10 mol% D$_2$O (C) and pure H$_2$O (D). The difference spectra in c) and d) have been derived from the spectra in a) and b), respectively. e) The ion-perturbed O–D stretching bands derived from c) and d).

follows[17)]

$$fwhm_i = 0.6436(w_{i,1} + w_{i,2}), \qquad (5)$$

and

$$Area_i = \pi h_i(w_{i,1} + w_{i,2})/4. \qquad (6)$$

The fitting procedure is done using the SALS program.[28)] The physical significance for the use of such an asymmetric function in the Raman spectrum has not been established. However, it can obviously be pointed out that the observed total O–D stretching band is poorly reproduced by the sum of symmetric Gaussian components in comparison with the asymmetric profile functions described here.

Results and Discussion

Figure 2 gives the result of the least squares fitting procedure for the isotropic spectrum of 4 mol% Zn(ClO$_4$)$_2$ aqueous solution at 26 °C. The O–D stretching band in the spectrum is satisfactorily reproduced by the sum of three contributions, (a) the band component centered at ca. 2650 cm^{-1} and (b) that at ca. 2400 cm^{-1}, and (c) that from HDO molecules in the bulk state. The 2650 cm^{-1} component has frequently been observed in Raman spectra in solutions containing ClO$_4^-$, and assigned to the contribution from HDO molecules interacting with ClO$_4^-$ by Walrafen.[7,8)] The position of peak a is in good agreement with the O–D stretching vibrational frequency of HDO molecules coordinated to ClO$_4^-$ determined by infrared double-difference studies.[15,17,21—23)] Thus, we can reasonably assign the peak a to the O–D stretching band from HDO molecules in the first hydration shell of ClO$_4^-$. The curve-slope at the low-frequency side of the total O–D stretching band does not apparently fit to that in the spectrum of pure water (denoted by c in Fig. 2). This deviation can be explained to occur owing to the presence of a weak and broadened component centered around 2400 cm^{-1} (peak b). The peak position of this component also agrees with the O–D stretching vibrational frequency of HDO molecules coordinated to Zn^{2+} (2427 cm^{-1}) as measured by infrared double-difference studies.[16,22)] We then assign the peak b to the contribution from HDO molecules in the first hydration shell of Zn^{2+}. Observed anisotropic spectra can be analyzed by the same procedure as that for isotropic ones described

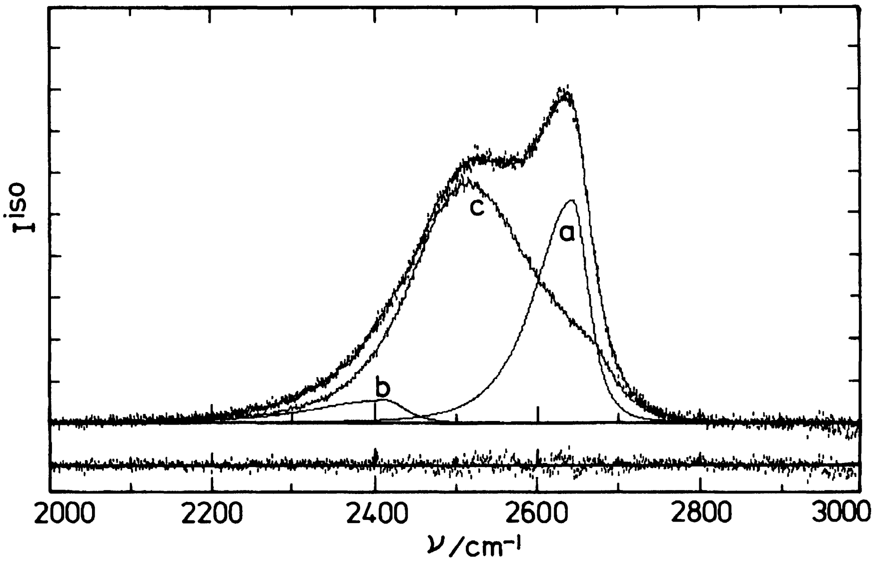

Fig. 2. Uncoupled O–D stretching band for aqueous 4 mol% $Zn(ClO_4)_2$ solution containing 10 mol% D_2O (dots). Band components (a) and (b) indicate the ClO_4^-- and Zn^{2+}-perturbed bands, respectively. c) The O–D stretching band for 10 mol% D_2O solution in H_2O. The residual functions (dots) are shown below.

above.

Figures 3 and 4 represent the temperature dependence of the uncoupled O–D stretching Raman band in both isotropic and anisotropic spectra of 4 mol% $Zn(ClO_4)_2$ aqueous solution, respectively. Band parameters decided by the least squares fitting procedure are listed in Table 1. In all temperatures investigated the observed total O–D stretching band is reproduced well by the sum of contributions from HDO molecules coordinated to the respective ions and that from HDO molecules belonging to the bulk water. Values of the full width at half-maximum position for the ion-perturbed

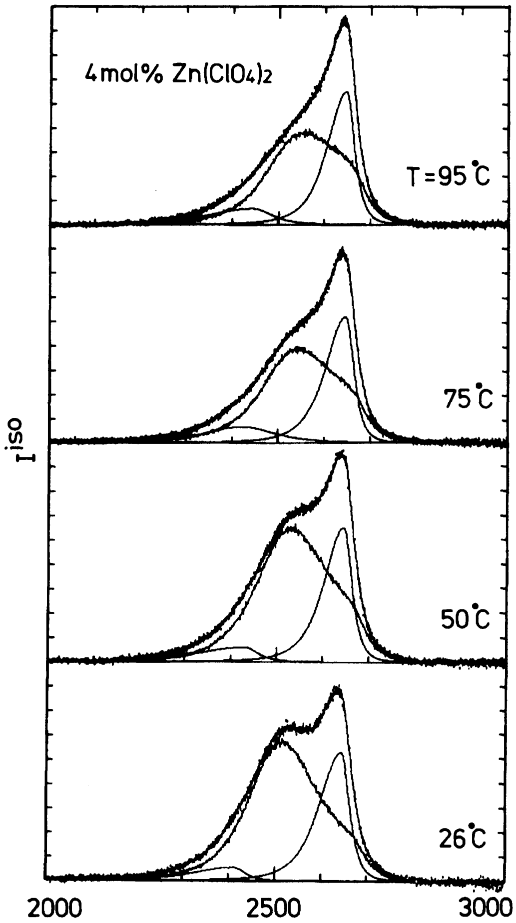

Fig. 3. Temperature dependence of the isotropic Raman spectra for aqueous 4 mol% $Zn(ClO_4)_2$ solution. The contributions from Zn^{2+}- and ClO_4^--perturbed bands and from the bulk O–D stretching band are indicated by solid lines.

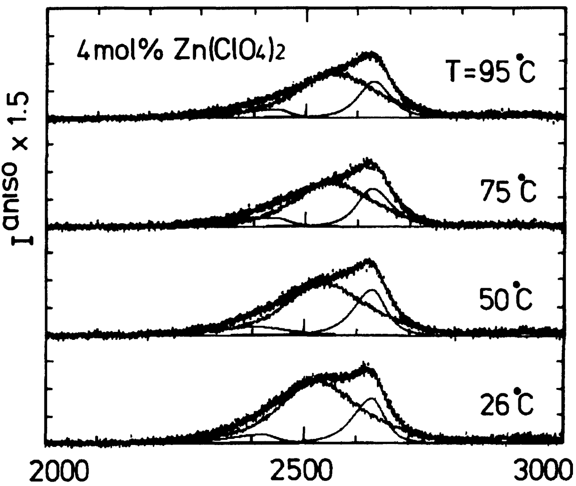

Fig. 4. Temperature dependence of the anisotropic Raman spectra for aqueous 4 mol% $Zn(ClO_4)_2$ solution. The contributions from Zn^{2+}- and ClO_4^--perturbed bands and from the bulk O–D stretching band are indicated by solid lines.

Table 1. The Position, the Full Width at Half Maximum, Area, and the Relative Integrated Intensity of Ion–Water Bands Derived from the Least Squares Fit of the Isotropic and Anisotropic Raman Difference Spectra for Aqueous 4 and 2 mol% $Zn(ClO_4)_2$ Solutions at Various Temperatures, ν, *fwhm*, *Area*, and B, Respectively[a)]

	t	Polarization	$Zn^{2+}\cdots HDO$ interaction				$ClO_4^-\cdots HDO$ interaction			
x	°C	mode	ν_+/cm^{-1}	$fwhm_+/cm^{-1}$	$Area_+/cm^{-1}$	B_+	ν_-/cm^{-1}	$fwhm_-/cm^{-1}$	$Area_-/cm^{-1}$	B_-
0.04	26	Isotropic	2413(15)	131(27)	43(9)	0.17(4)	2642(1)	77(2)	250(8)	1.44(5)
		Anisotropic	2425(5)	103(9)	13(1)	0.20(2)	2631(1)	70(1)	46(1)	1.11(3)
	50	Isotropic	2431(14)	152(28)	55(11)	0.22(4)	2644(1)	71(2)	241(8)	1.44(5)
		Anisotropic	2407(3)	157(7)	19(1)	0.35(2)	2630(1)	72(1)	48(1)	1.33(2)
	75	Isotropic	2440(11)	133(18)	46(7)	0.22(3)	2646(1)	66(2)	212(5)	1.56(5)
		Anisotropic	2443(5)	153(9)	19(1)	0.42(3)	2627(1)	75(2)	42(1)	1.37(4)
	95	Isotropic	2453(11)	145(17)	53(7)	0.28(4)	2647(1)	65(1)	211(5)	1.67(5)
		Anisotropic	2448(2)	141(6)	16(1)	0.34(2)	2632(1)	70(2)	37(1)	1.18(3)
0.02	26	Isotropic	2388(10)	94(20)	13(3)	0.10(2)	2645(2)	79(3)	135(5)	1.54(6)
		Anisotropic	2423(5)	145(10)	8.4(7)	0.29(3)	2638(2)	84(2)	30(1)	1.54(5)
	50	Isotropic	2409(10)	121(20)	18(4)	0.14(3)	2649(2)	74(3)	125(5)	1.50(6)
		Anisotropic	2423(7)	142(9)	9(1)	0.35(4)	2635(1)	75(4)	25(1)	1.42(5)
	75	Isotropic	2420(8)	142(17)	27(4)	0.23(3)	2649(2)	65(3)	117(5)	1.47(6)
		Anisotropic	2421(9)	192(11)	12(1)	0.58(5)	2634(3)	74(4)	25(2)	1.7(1)
	95	Isotropic	2433(7)	139(21)	30(4)	0.26(3)	2650(1)	62(2)	123(5)	1.56(6)
		Anisotropic	2429(4)	135(21)	9(2)	0.46(7)	2638(2)	80(3)	24(1)	1.74(7)

a) Estimated standard deviations are given in parentheses.

O–D stretching bands at 26 °C are in reasonable agreement with those measured by infrared double-difference studies.[15,16,22)] No marked temperature dependence of band parameters were found for Zn^{2+} and ClO_4^--perturbed O–D components, although the full width of the isotropic O–D stretching band perturbed by ClO_4^- slightly decreased with increasing temperature. A big change in the shape of the total O–D stretching band against temperature in Fig. 3 is mainly due to a considerable variation in the bulk component with increasing temperature. This may be considered to reflect the weakness or breakdown of hydrogen-bonds between the bulk water molecules in the solution by the elevation of temperature.

It has been reported in an X-ray diffraction study that a stable octahedral aqua-complex, $Zn(H_2O)_6^{2+}$, is formed in a 4.1 mol% $Zn(ClO_4)_2$ aqueous solution at 25 °C.[29)] Further, a neutron diffraction study using $^{35}Cl/^{37}Cl$ isotopic substitution has shown that there are 4.5±0.5 water molecules neighboring the ClO_4^- ion in a 6.1 mol% $NaClO_4$–D_2O solution.[30)] The local configuration of ClO_4^- and the neighboring water molecules is suggested to be described as one of hydrogen atoms of each water molecule neighboring the ion is facing an oxygen atom of ClO_4^-. Our Raman scattering result may also suggest that these local structures around Zn^{2+} and ClO_4^- are sufficiently retained at 26—95 °C. It is known that most of the water molecules in pure liquid water form a 4-fold complete hydrogen-bonded network structure at room temperature.[31)] These hydrogen bonds are gradually broken down with increasing temperatures, and then the fraction of 3- or 2-fold hydrogen-bonded water molecules is increased. The fraction of these incompletely hydrogen-bonded molecules may be seen by an increase in the high-frequency component of the O–H stretching band in pure water. The $Zn^{2+}\cdots$water interaction is considered to be much stronger than that between bulk water molecules. This strong interaction remains unchanged at the higher temperature of 95 °C. On the other hand, the $ClO_4^-\cdots$water interaction is much weaker already at room temperature than that between bulk molecules despite of the presence of a defined first hydration shell.[30)] To examine the influence of the ion–water interaction on the polarizability of HDO molecule, the relative integrated intensity of two ion-perturbed bands is estimated as below.

The relative integrated scattering intensity from HDO molecules coordinated to Zn^{2+} and ClO_4^-, B_+ and B_-, can be calculated using the observed Raman band area and hydration number of Zn^{2+} and ClO_4^- from the diffraction study, that is to say,

$$B_+=[Area_+/(n_{+,H_2O}\cdot x)]/[C_{bulk}/\{(1-x)-(n_{+,H_2O}+1/2\cdot n_{-,H_2O})x\}], \tag{7}$$

and

$$B_-=[Area_-/(n_{-,H_2O}\cdot x)]/[C_{bulk}/\{(1-x)-(n_{+,H_2O}+1/2\cdot n_{-,H_2O})x\}], \tag{8}$$

where, n_{i,H_2O} and x are the hydration number of ion i and the mole fraction of $Zn(ClO_4)_2$, respectively. Values $n_{+,H_2O}=6$ and $n_{-,H_2O}=4$ are taken for this solution. C_{bulk} denotes the integrated scattering intensity from bulk HDO molecules. In the case where the scattering intensity from HDO molecules coordinated to the ion is identical to that from bulk molecules, the value of B_i should be unity according to Eqs. 7 and 8. These values of B_+ obtained in the 4 mol% $Zn(ClO_4)_2$ solution are found to be much smaller than 1.0 for both the isotropic and anisotropic spectrum as shown in Table 1. This implies that the deformation of the electron cloud in these HDO molecules is considerably restricted due to the stronger $Zn^{2+}\cdots OHD$ interaction during the vibrational motion. On the contrary, the relative integrated intensity from ClO_4^--perturbed HDO molecules is much larger than 1.0, indicating that a considerable change of their polarizability occurs during the O–D stretching vibrational motion. In addition, it must be pointed out that there is a significant difference in the value of B_- between isotropic and anisotropic spectra. Consequently, it is suggested that the depolarization ratio of ClO_4^--perturbed HDO molecules is smaller than that of bulk HDO molecules in the aqueous solution.

Figures 5 and 6 show the results of uncoupled O–D stretching band components at respective temperatures in 2 mol% $Zn(ClO_4)_2$ aqueous solution. Peak parameters found by the least squares fitting procedure are included in Table 1. In spite of the smaller contribution from ion-perturbed HDO molecules compared with that in the 4 mol% $Zn(ClO_4)_2$ solution because of the smaller amount of solute, the observed total O–D stretching band is again well reproduced by the sum of contributions from Zn^{2+} perturbed-, ClO_4^- perturbed-, and bulk-HDO molecules in the 2 mol% solution. Uncertainties involved in the band parameters of anisotropic spectra are slightly larger than those in the 4 mol% $Zn(ClO_4)_2$ solution, perhaps due to the limited statistical accuracy. Nevertheless, similar conclusions can be drawn for the 2 mol% $Zn(ClO_4)_2$ solution as discussed for the 4 mol% $Zn(ClO_4)_2$ solution. Band parameters obtained for the former solution agree reasonably with those for the latter. The same result for both solutions with different solute concentrations may show the validity of this double-difference analysis for Raman spectra.

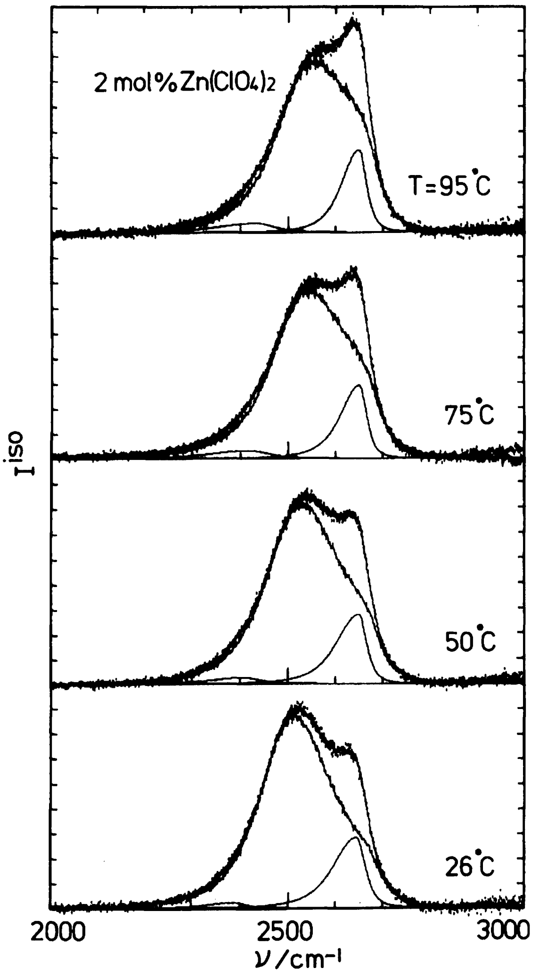

Fig. 5. Same notations as in Fig. 3 except for aqueous 2 mol% $Zn(ClO_4)_2$ solution.

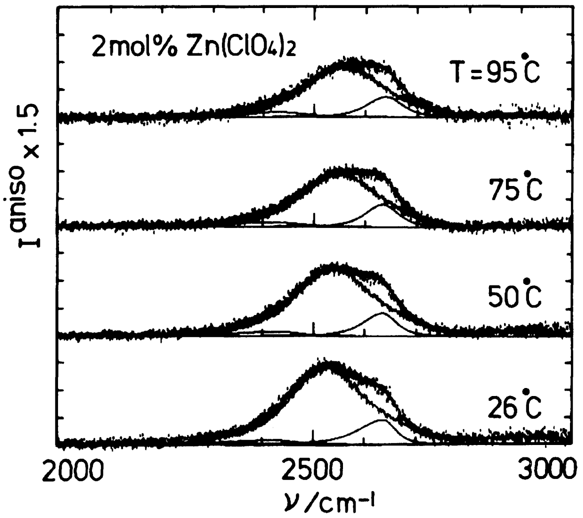

Fig. 6. Same notations as in Fig. 4 except for aqueous 2 mol% $Zn(ClO_4)_2$ solution.

In summary, the following facts have become apparent through the double-difference analysis of these Raman spectrum data for $Zn(ClO_4)_2$ aqueous solutions: the polarizability of HDO molecules in the first coordination shell of Zn^{2+}, estimated from the relative integrated Raman scattering intensities, does not significantly change during the O–D stretching vibrational motion, reflecting a strong interaction between $Zn^{2+}\cdots OHD$. A considerable change of the polarizability and increase of the depolarization ratio are observed for HDO molecules neighboring with ClO_4^-. No marked temperature dependence in the range 26—95 °C were found from these analyses concerning the interaction between the constituent ion and the neighboring water molecules. At any rate, it has been indicated that the double-difference Raman spectroscopy can provide detailed information on the vibrational motion of H_2O molecules, particularly, in the first coordination shell of the constituting ion in aqueous solution. Furthermore, this method can give new information on the electronic state of H_2O molecules interacting with the constituent ion in the solution.

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