The Intramolecular Structure of Oxonium Ion in Concentrated Aqueous Deuterochloric Acid Solutions

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(Received March 12, 1992)

Time-of-flight (TOF) neutron diffraction experiments have been carried out for pure liquid D_2O and concentrated aqueous deuterochloric acid solutions $(DCl)_x(D_2O)_{1-x}$ (x=0.10, 0.23). The errors due to the inelasticity effect on the molecular structure in the solution were markedly reduced by the TOF measurement at the small scattering angle (2θ=44°). From the least square fit of the theoretical intramolecular interference function to the observed one, the internuclear distances, r_{OD} and r_{DD}, and the root mean square displacements, l_{OD} and l_{DD}, in both D_3O^+ and D_2O molecules were determined as follows; r_{OD}=1.04(4) Å, r_{DD}=1.63(5) Å, l_{OD}=0.07(2) Å and l_{DD}=0.12(6) Å for D_3O^+, and r_{OD}=0.983(5) Å, r_{DD}=1.55(4) Å, l_{OD}=0.067(8) Å, and l_{DD}=0.12(4) Å for D_2O. The bond angle ∠DOD in D_3O^+ was also calculated to be 103°. The trigonal pyramidal structure of oxonium ion in the liquid phase has been lead through this investigation.

Oxonium ion is one of the most important chemical species in extensive fields of the science. The existence of a single or hydrated oxonium ions in the crystalline state is well-known by a number of X-ray and neutron diffraction experiments.[1-6] The molecular structure of oxonium ion in $HCl\cdot H_2O$[1] and $HClO_4\cdot H_2O$[2] crystals has been proposed to be a trigonal pyramid. This molecular geometry has been confirmed by the exact neutron diffraction analysis for *p*-toluenesulfonic acid monohydrate crystals,[3] indicating that the average O–H distance in H_3O^+ and the bond angle were determined to r_{OH}=1.011 Å and ∠HOH=110.4°, respectively. On the other hand, the molecular structure of an isolated H_3O^+ has been reported to be a planar equilateral triangle according to the ab initio molecular orbital calculation.[7]

The molecular geometry of this ion in the liquid state remains less clear at present, although various interpretations about the molecular geometry of H_3O^+ in the solution have been hitherto made. For instance, the Raman spectrum of molten $HClO_4\cdot H_2O$[8] at 55 °C has indicated the same fundamental vibrational modes of a pyramidal H_3O^+ as observed in the low temperature crystalline phase. ^{1}H NMR spectra from the partially deuterated oxonium ion in 'super-acid' media have evidenced three equivalent protons in H_3O^+. The ^{17}O–^{1}H coupling constant obtained from ^{17}O NMR spectra of $H_3{}^{17}O^+$ in liquid SO_2 has suggested the sp^2 hybridization of oxygen atom in H_3O^+,[10] leading to the planar molecular structure. X-Ray diffraction studies on the solution containing H_3O^+ have indicated considerably short $H_3O^+\cdots H_2O$ distances (2.56 Å,[11] 2.44 Å[12]), in comparison with $H_2O\cdots H_2O$ distance (2.8 Å [13-15]) in the liquid water, which implies the strong interaction between H_3O^+ and water molecules may exist in the first hydration shell around the ion. Lee et al.[12] have proposed hydration model of H_3O^+, in which H_3O^+ is strongly bonded to three water molecules and is weakly interacted with one water molecule. They have also noted the almost planar triangle structure of $H_3O^+(H_2O)_3$ unit. Unambiguous information on the molecular structure of the oxonium ion in the liquid phase may be given from neutron and X-ray diffraction experiments. In fact, the results of time-of-flight (TOF) neutron diffraction measurement on 1 M DCl and DBr (1 M=1 mol dm^{-3}) aqueous solutions[16] has exhibited the tetrahedral hydration around D_3O^+. However, the intramolecular structure of D_3O^+ in these measurements could not be directly obtained. The tetrahedral hydration structure has also been reported from X-ray and neutron diffraction analyses of aqueous HCl(or DCl) solutions in the extended concentration range by Triolo and Narten.[17] According that the bond angle ∠DOD=104.5° which corresponds to the value of H_2O molecule found in gaseous state,[18] they obtained r_{OD}=1.017 Å and r_{DD}=1.608 Å as the intramolecular distances in D_3O^+ from the diffraction data of $DCl\cdot 3.08D_2O$ solution.

The difficulty in determining the reliable molecular structure in the solution by neutron diffraction experiments mainly arises from the inelasticity effect included in the intramolecular interference term.[19-22] Particularly, for the liquid samples which contain light nucleus such as deuteron, this effect becomes considerably large especially in the measurement at high scattering angles which are essential to the steady state reactor experiments using slow incident neutrons. The most serious problem caused by this effect is the 'apparent shrinkage' in the inter-atomic distance in the molecule. The apparent shrinkage is roughly proportional to $\sin^2\theta$ (θ: the scattering angle). For example, more recent structural analyses making the inelasticity corrections for both the self scattering and intramolecular interference terms has given 0.97—0.98 Å[20-22] as r_{OD} in D_2O in pure liquid D_2O, which is compared with r_{OD}=0.955 Å without the correction proposed by Triolo and Narten. The inelasticity effect may be expected to be reduced experimentally by the diffraction measurement fixed at the small scattering angle and using incident neutrons of short wavelength. Therefore, one of the most possible method satisfying this condition is to apply the TOF neutron diffraction measurement at the small scattering angle.

In this study, we describe on the experimental results of TOF neutron diffraction on concentrated aqueous DCl solutions, for the purpose of determining the molecular geometry of the oxonium ion in the liquid phase.

Theory

The observed coherent scattering cross section derived from the neutron diffraction experiment is divided into two contributions, namely, self and interference terms, the latter of which contains all the information concerning the liquid structure.[23] The self term scaled by a stoichiometric unit, $(\mathrm{DCl})_x(\mathrm{D_2O})_{1-x}$, is written as

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{self}}=\Sigma c_i b_i^2=(2-x)b_{\mathrm{D}}^2+(1-x)b_{\mathrm{O}}^2+xb_{\mathrm{Cl}}^2, \tag{1}$$

where c_i and b_i denote the number of nucleus i in the stoichiometric unit and the coherent scattering length of nucleus i, respectively. The interference term consists of both the intra- and intermolecular contributions. The intramolecular interference term, which is a linear combination of the scattering from isolated D_2O and D_3O^+, can be expressed as

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{intra}}=(1-2x)(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{intra}}(\text{for } \mathrm{D_2O}) + x(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{intra}}(\text{for } \mathrm{D_3O^+}), \tag{2}$$

where,

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{intra}}(\text{for } \mathrm{D_2O})=4b_{\mathrm{O}}b_{\mathrm{D}}\exp(-l_{\mathrm{OD1}}{}^2Q^2/2)\frac{\sin(Qr_{\mathrm{OD1}})}{Qr_{\mathrm{OD1}}} + 2b_{\mathrm{D}}^2\exp(-l_{\mathrm{DD1}}{}^2Q^2/2)\frac{\sin(Qr_{\mathrm{DD1}})}{Qr_{\mathrm{DD1}}} \tag{3}$$

and

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{intra}}(\text{for } \mathrm{D_3O^+})=6b_{\mathrm{O}}b_{\mathrm{D}}\exp(-l_{\mathrm{OD2}}{}^2Q^2/2)\frac{\sin(Qr_{\mathrm{OD2}})}{Qr_{\mathrm{OD2}}} + 6b_{\mathrm{D}}^2\exp(-l_{\mathrm{DD2}}{}^2Q^2/2)\frac{\sin(Qr_{\mathrm{DD2}})}{Qr_{\mathrm{DD2}}}. \tag{4}$$

In these equations, l_{ijk} and r_{ijk} represent the root mean square displacement and the internuclear distance of nuclear pair i–j in D_2O ($k=1$) and in D_3O^+ ($k=2$), respectively. The intermolecular interference term is given by the weighted sum of six partial structure factors, $a_{ij}(Q)$, as below,

$$\begin{aligned}(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{inter}}=&(2-x)^2b_{\mathrm{D}}^2(a_{\mathrm{DD}}(Q)-1)\\&+(1-x)^2b_{\mathrm{O}}^2(a_{\mathrm{OO}}(Q)-1)\\&+x^2b_{\mathrm{Cl}}^2(a_{\mathrm{ClCl}}(Q)-1)\\&+2(2-x)(1-x)b_{\mathrm{D}}b_{\mathrm{O}}(a_{\mathrm{OD}}(Q)-1)\\&+2x(2-x)b_{\mathrm{D}}b_{\mathrm{Cl}}(a_{\mathrm{DCl}}(Q)-1)\\&+2x(1-x)b_{\mathrm{O}}b_{\mathrm{Cl}}(a_{\mathrm{OCl}}(Q)-1).\end{aligned} \tag{5}$$

The Fourier transform of $(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{inter}}$ gives the intermolecular distribution function $g^{\mathrm{inter}}(r)$,

$$g^{\mathrm{inter}}(r)=1+\frac{1}{2\pi^2\rho_0 r}\int_0^{Q_{\max}}\frac{(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{inter}}}{(\Sigma\, c_i b_i)^2}\,Q\sin(Qr)\,\mathrm{d}Q. \tag{6}$$

Experimental

Materials. Pure D_2O (99.8 atom% D) and 23 mol% DCl solution in D_2O (>99 atom% D) were obtained from Merck Co., Ltd. 10 mol% DCl solution in D_2O was prepared by the dilution of 23 mol% DCl solution by adding the weighted amount of D_2O. The sample solutions were sealed into a cylindrical thin walled fused quartz cell with 8 mm in inner diameter and 0.4 mm in wall thickness. The sample parameters used are listed up in Table 1.

Neutron Diffraction Measurement. TOF neutron diffraction measurements were performed at 25 °C using a total scattering instrument HIT[24] for high intensity beam installed at the pulsed spallation neutron source (KENS) in National Laboratory for High Energy Physics, Tsukuba, Japan. Measurements were made in advance for an empty cell, background and a vanadium rod which has the same dimension as the sample. The scattered neutrons were detected by ^{3}He counters located at respective scattering angles of 2θ=8, 14, 25, 32, 44, 91, and 150°.

Data Reduction. The measured scattering data were corrected for the background, absorption[25] and multiple[26] and incoherent scatterings. The observed count rate for each sample was converted to the absolute scale using scattering intensities from the vanadium rod. The normalized scattering cross sections which are corrected except for the inelasticity effect, for 23 mol% DCl solution are shown in Fig. 1. The observed cross sections at small scattering angles below 44° exhibit almost a similar oscillation amplitude around the static limit $\Sigma c_i b_i^2$, indicating that the inelasticity effect in the self term is sufficiently small at lower angles. Therefore, the distortion for a functional form of the interference term is expected to be negligible at these angles.[19,20] Much greater deviations from the static limit in addition to obscurity in oscillation amplitude of the interference can be observed in 91° and 150° data. A little difference in the shape of interference terms between the data at low angles may be considered to be mainly due to the difference in the instrumental resolution.

Table 1. The Number of Atom c_i, Mean Scattering and Absorption Cross Sections and the Number Densities Scaled in the Stoichiometric Unit $(\mathrm{DCl})_x(\mathrm{D_2O})_{1-x}$ for Samples Used in This Study

Samples	c_{D}	c_{H}	c_{O}	c_{Cl}	σ_s/barns	σ_a/barns[a)]	ρ_0/Å^{-3}
$(\mathrm{DCl})_{0.23}(\mathrm{D_2O})_{0.77}$	1.752	0.018	0.770	0.230	21.959	4.285	0.0320
$(\mathrm{DCl})_{0.10}(\mathrm{D_2O})_{0.90}$	1.890	0.010	0.900	0.100	20.735	1.864	0.0331
D_2O	1.996	0.004	1.000	—	19.805	0.002	0.0333

a) For the incident neutron wavelength of 1 Å.

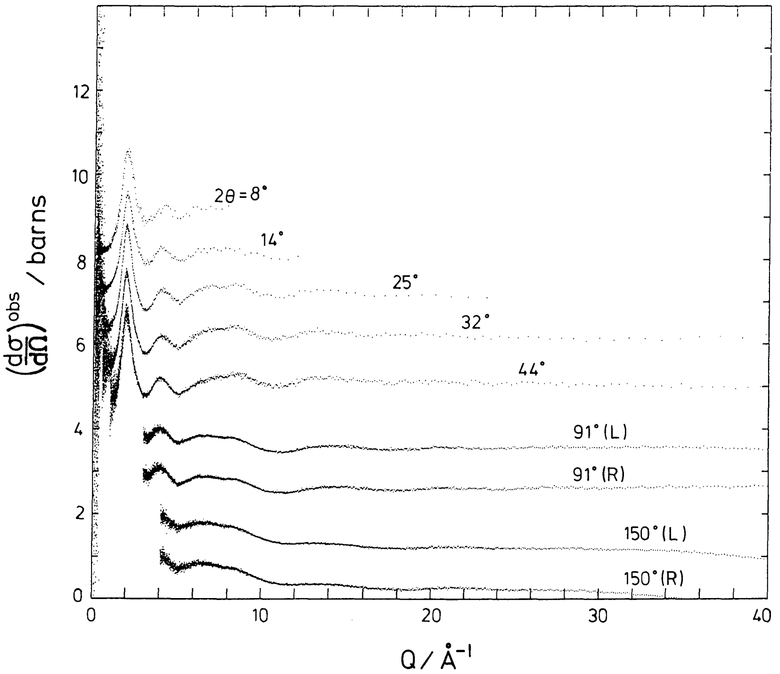

Fig. 1. The observed total scattering cross sections for 23 mol% DCl solution in D_2O at 25 °C. R and L denote detectors located at the right- and left-hand sides of the incident neutron beam, respectively.

The distortion of the functional form by the instrumental cause tends to become more with decreasing the scattering angle.[27] Consequently, taking into consideration of minimizing both the inelasticity and instrumental effects, we will adopt only the data at $2\theta=44°$ for the subsequent structural analysis. Even if strong correlations between constituent molecules may exist in the solution, the value of the intermolecular interference term decays to be null much faster than that of the intramolecular term because of relatively large internuclear distances and root mean square amplitudes for the intermolecular contribution. Therefore, the oscillating pattern of diffraction data in the high-Q region ($Q=4\pi/\lambda \sin\theta$) is decisively characterized by the intramolecular contribution. The detailed molecular geometries of D_2O and D_3O^+ can be determined by the least square fit of Eq. 2 to the observed interference term in the Q-region of $8<Q<25$ Å^{-1}. Prior to fitting, it should be necessary to correct low frequency systematic errors of the observed interference term, which is mainly arised from a little distortion in the self scattering term by the inelasticity effect. This correction is achieved in the following procedure.

(1) The smoothed observed total interference term is converted to the total distribution function $g(r)$ through the Fourier transformation. Unphysical oscillations of the total $g(r)$ in the subatomic region of r are eliminated and afterwards, the total $g(r)$ is back-transformed to obtain the corrected interference term.

(2) Secondary, after subtracting this term from the observed total scattering cross section, the resultant self scattering contribution including errors is extensively smoothed. The smoothed self term indicates no sudden fluctuations and becomes almost flat in the region of $Q>6$ Å^{-1}, where the intramolecular contribution is dominant.

(3) This smoothed self term is subtracted from the observed total scattering cross section. In this way, we obtain the fully corrected experimental total interference term.

Results and Discussion

Intramolecular Structure of D_2O. The corrected total interference term for pure liquid D_2O , shown in Fig. 2 is almost similar to the previous data from reactor[20,29–32] and time-of-flight[33–35] experiments. Two internuclear distances, r_{OD} and r_{DD}, and two root mean square displacements, l_{OD} and l_{DD}, for D_2O molecule can be determined through the least square fit of Eq. 3 to the observed interference term of liquid D_2O in the range of $8<Q<25$ Å^{-1}. The fitting was performed by using the SALS program,[28] assuming that the statistical error distributes uniformly over the whole range of Q. The molecular parameters determined are respectively $r_{OD}=0.983\pm0.005$ Å, $r_{DD}=1.55\pm0.04$ Å, $l_{OD}=0.067 \pm0.008$ Å, and $l_{DD}=0.12\pm0.04$ Å for D_2O in the liquid phase at 25 °C. The bond angle ∠DOD in D_2O is also estimated to be 104±5°. These parameters are listed and compared with several literature values in Table 2. The values of intramolecular distances determined in this study agree well with those from earlier studies in which the inelasticity correction for the intramolecular interference term has been made. The structural data without this correction, except for Soper's work by the small scattering angle TOF method,[38] give considerably shorter intramolecular distances and larger root mean square displacements than the values predicted from the

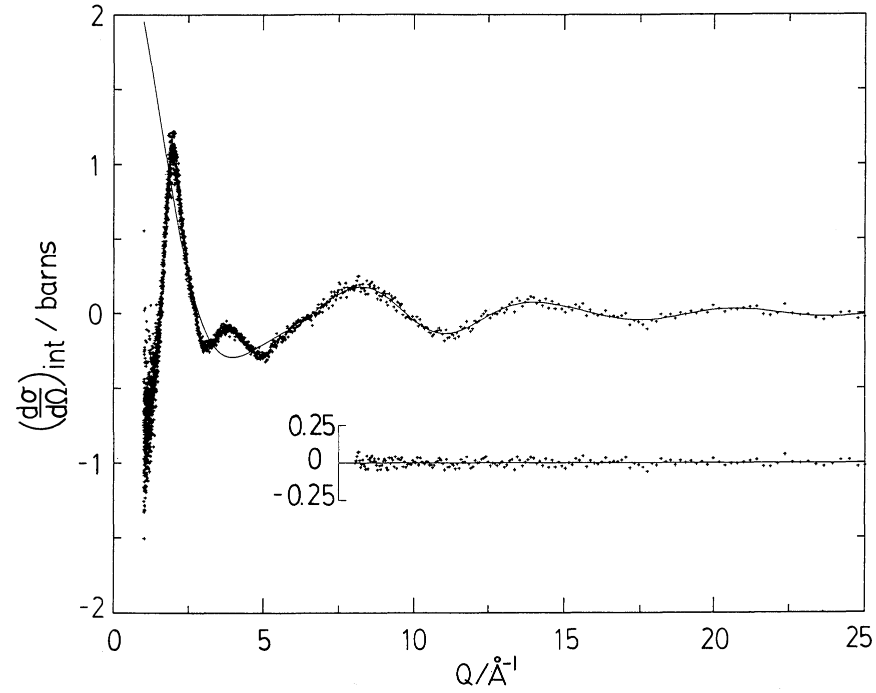

Fig. 2. The observed total interference term (dots) and the best fit with the intramolecular interference term of Eq. 2 (solid line) at $2\theta=44°$ for liquid D_2O. The residual function (dots) is shown below.

Table 2. The Comparison of Molecular Parameters of D_2O in the Liquid Phase Determined from the Neutron Diffraction Experiments

Authors	r_{OD}/Å	l_{OD}/Å	r_{DD}/Å	l_{DD}/Å	Experimental method	Applied inelasticity correction for interference term?
Narten (1972)[36]	0.934(4)	0.138(4)	1.53(3)	0.24(2)	Reactor	No
Powles (1973)[37]	0.96	—	—	—	TOF ($2\theta=150°$)	No
Triolo and Narten (1975)[17]	0.955(5)	0.143(5)	(1.510)[a]	0.235(5)	Reactor	No
Walford et al. (1977)[29]	0.98(1)	—	1.56(3)	—	Reactor	Yes[c]
Powles (1981)[20]	0.983(8)	(0.0588)[b]	1.55(2)	(0.101)[b]	Reactor[d]	Yes
Thiessen and Narten (1982)[30]	0.966(6)	0.095(5)	1.51(3)	0.09(2)	Reactor	Yes
Soper (1986)[38]	0.98	0.07	1.56	0.07	TOF ($2\theta=40°$)	No
Kameda and Ichikawa (1986)[35]	0.971(3)	(0.0588)[b]	1.55(2)	(0.101)[b]	TOF ($2\theta=91°$)	Yes
Bellissent-Funel et al. (1991)[32]	0.989	0.059	1.583	0.087	Reactor	Yes[c]
Ichikawa et al. (1991)[22]	0.970(5)	(0.0588)[b]	1.55(1)	(0.101)[b]	TOF ($2\theta=91°$)	Yes
This work	0.983(5)	0.067(8)	1.55(4)	0.12(4)	TOF ($2\theta=44°$)	No

a) Calculated value from r_{OD} by assumption that the DOD bond angle has the same value as in the vapor phase (=104.5°). b) Calculated value from the fundamental vibrational frequencies of D_2O molecule in the liquid phase. c) Approximate kinematical correction for the interference term has been applied. d) Data from Walford et al. (1977).[29]

vibrational frequencies of D_2O molecule in the liquid phase,[20] as listed up in Table 2. These results point out that the inelasticity effect can fully be neglected by the present experimental condition, that is, the TOF method at the small scattering angle. For the structure determination of D_3O^+ mentioned below, it is essential to obtain precise intramolecular parameters for D_2O, because relatively small errors in the parameters for D_2O produce considerable uncertainties in molecular parameters for D_3O^+ through the least square fitting procedure using Eq. 2.

Intramolecular Structure of D_3O^+. It can be reasonably expected that D_3O^+ molecule has a longer OD distance than D_2O molecule through a preliminary analysis of the difference distribution function defined as the Fourier transform of the below equation,

$$(d\sigma/d\Omega)_{int}(\text{for DCl solution}) \\ -(1-2x)(d\sigma/d\Omega)_{int}\ (\text{for pure } D_2O), \qquad (7)$$

where $(d\sigma/d\Omega)_{int}$ denotes observed total interference term and x is the mole fraction of DCl in the solution.

The contribution from the intramolecular structure of D_2O is canceled in Eq. 7, at least, in the intramolecular range of r, i.e., $r<1.5$ Å. The position of the first peak in the Fourier transform of Eq. 7, corresponding to the intramolecular OD distance in D_3O^+ is located at 1.04 Å, while, the corresponding peak position in D_2O molecule from pure D_2O is 0.98 Å.

The molecular parameters for D_3O^+ can be determined by the least square fit of Eq. 3 involving both the contributions from D_3O^+ and D_2O to the observed total interference term of 23 mol% DCl solution as shown in Fig. 3. The inelasticity effect for the intramolecular interference term in the data can be again postulated to be sufficiently small in this work. The structure parameters for D_2O molecule in this solution are assumed to be the same as the values from pure D_2O data. The OD and DD distances in D_3O^+ with their root mean square displacements l_{OD} and l_{DD} are determined to be $r_{OD}=1.04\pm0.04$ Å, $r_{DD}=1.63\pm0.05$ Å, $l_{OD}=0.07\pm0.02$ Å, and $l_{DD}=0.12\pm0.06$ Å, respectively, through the similar fitting procedure. The bond angle, $\angle DOD=103\pm10°$, derived from these parameters obviously exhibits the trigonal pyramidal structure of oxonium ion in the solution. It is noteworthy that these parameters determined in this work were obtained without any assumption on the molecular geometry of D_3O^+. These parameters are listed and compared with the previous data in Table 3. The values of root mean square displacements for D_3O^+ agree well with those for D_2O molecule in Table 2. This agreement is reasonably supported from the fact that the molecular force constants for D_3O^+ is very similar to those for D_2O in the liquid phase according to the spectroscopic data.[8] The structure parameters for D_3O^+ in the liquid phase have been reported by Triolo and Narten, who give much larger l_{OD} and l_{DD} values than the present ones, because of no consideration for the inelasticity effect. They have also failed in determining the value of r_{DD} for D_3O^+ molecule through their least square analysis .[17]

The intramolecular interference term for 10 mol% DCl solution was calculated using the parameters for D_2O and D_3O^+ determined in this study without further

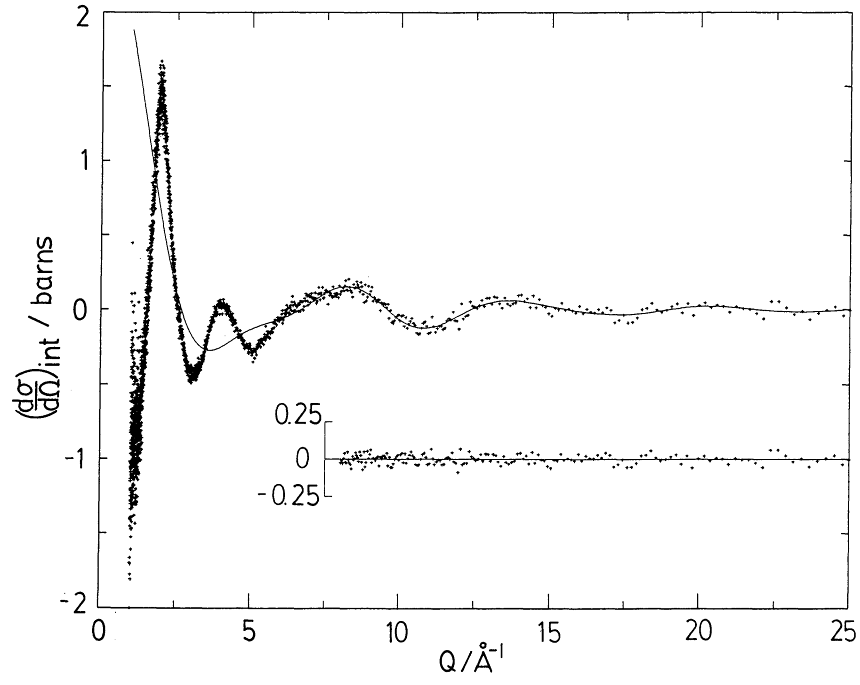

Fig. 3. The same notations as Fig. 2 except for 23 mol% DCl solution.

Table 3. Intramolecular Parameters of D_3O^+ (H_3O^+) in Solid and Liquid Phases

Authors	r_{OD}/Å	l_{OD}/Å	r_{DD}/Å	l_{DD}/Å	∠DOD/°	Phase	Experimental method
Yoon and Carpenter (1959)[1]	0.96(8)	—	(1.65)	—	117	Solid	X-Ray (single crystal)
Lundgren and Williams (1973)[3]	1.011(8)	—	(1.660)	—	110.4(5)	Solid	Neutron (single crystal)
O'Reilly et al. (1971)[39]	1.01(2)	—	1.74(3)	—	118.5(7)	Solid	NMR
Triolo and Narten (1975)[17]	1.017(5)	0.140(6)	(1.608)[a]	0.229(6)	(104.5)	Liquid	Neutron/Reactor
This work	1.04(4)	0.07(2)	1.63(5)	0.12(6)	103(10)	Liquid	Neutron/TOF ($2\theta=44°$)

a) Calculated value from r_{OD} by assumption that the DOD bond angle has the same value as in the vapor D_2O (=104.5°).

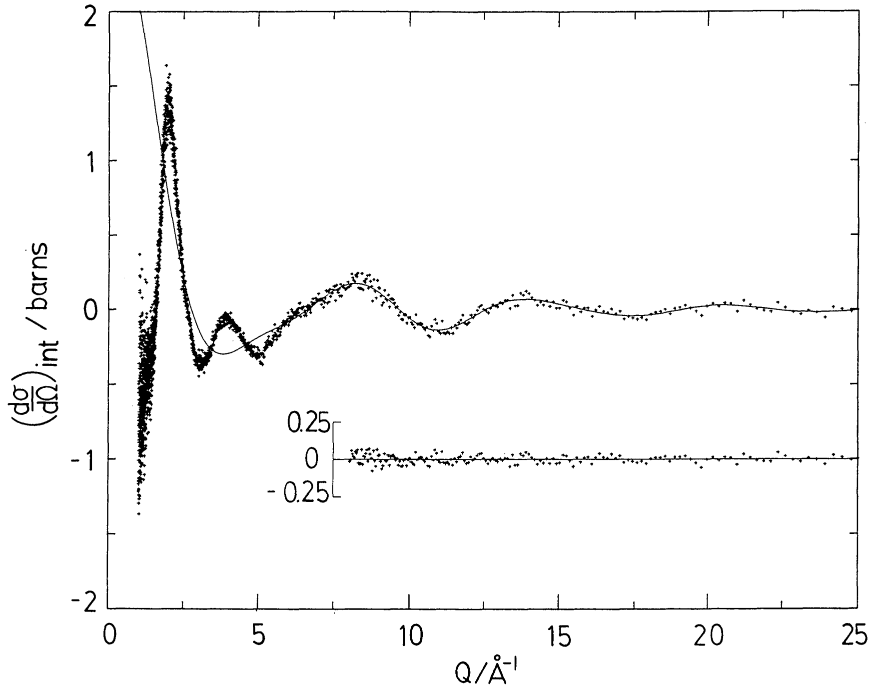

Fig. 4. The observed total interference term (dots) for 10 mol% DCl solution and intramolecular interference term calculated using molecular parameters obtained from the analysis of pure D_2O and 23 mol% DCl solution data.

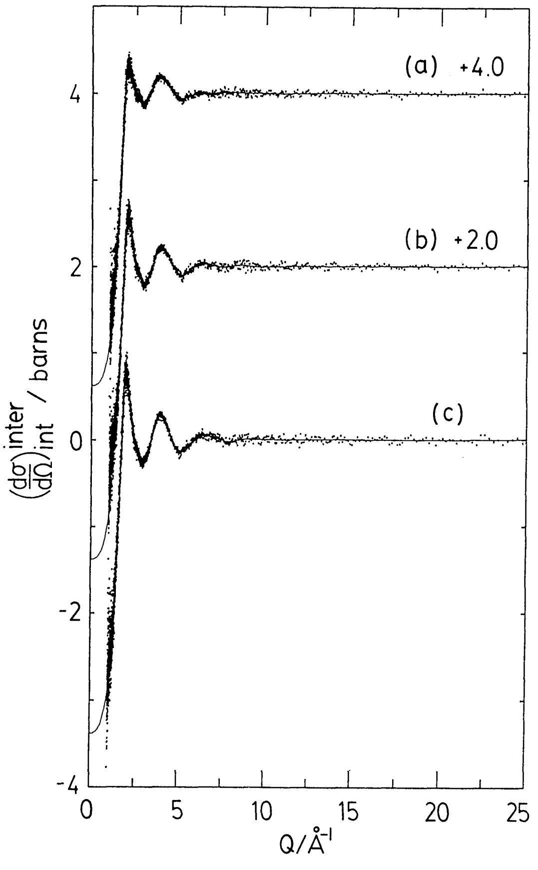

Fig. 5. The observed intermolecular interference terms (dots) for (a) liquid D_2O, (b) 10 mol% and (c) 23 mol% DCl solutions, respectively. Solid lines were used for the Fourier transform.

adjustments and is compared with the observed total interference term in Fig. 4. The calculated term agrees well with the observed one in the region of $Q>8$ Å^{-1}, indicating that the present structural analysis for both molecules are sufficiently reliable and that the molecular structure of D_2O and D_3O^+ remains unchanged in the concentration range covered.

Intermolecular Structure. The intermolecular interference term, $(d\sigma/d\Omega)^{inter}_{int}$, for each solution is derived by subtracting the calculated intramolecular contribution from the observed total interference term, which is denoted in Fig. 5. The oscillation amplitude of the interference seems to become stronger with increasing DCl concentration. The intermolecular distribution function $g^{inter}(r)$ is calculated by the Fourier transform of smoothed $(d\sigma/d\Omega)^{inter}_{int}$. In this calculation, observed $(d\sigma/d\Omega)^{inter}_{int}$ in the Q region with less than ca. 1 Å^{-1} was smoothly extrapolated to the Q=0 value. The value of $(d\sigma/d\Omega)^{inter}_{int}$ at Q=0 was evaluated by following relation,

$$(d\sigma/d\Omega)^{inter}_{int}(Q=0)=\sum c_i b_i^2(\rho_0\chi_T k_B T-1) - (d\sigma/d\Omega)^{intra}_{int}\ (Q=0), \quad (8)$$

where k_B and χ_T are the Boltzmann constant and the isothermal compressibility, respectively. Figure 6 describes the intermolecular distribution functions, $g^{inter}(r)$, truncated at $Q_{max}=20$ Å^{-1} for three samples. Small ripples existing in the region of $r<1$ Å may be associated with the truncation effect. It appears that the $g^{inter}(r)$ for pure D_2O is almost the same as the previous data.[17,32,35,40] Some part of the broad shoulder appear-

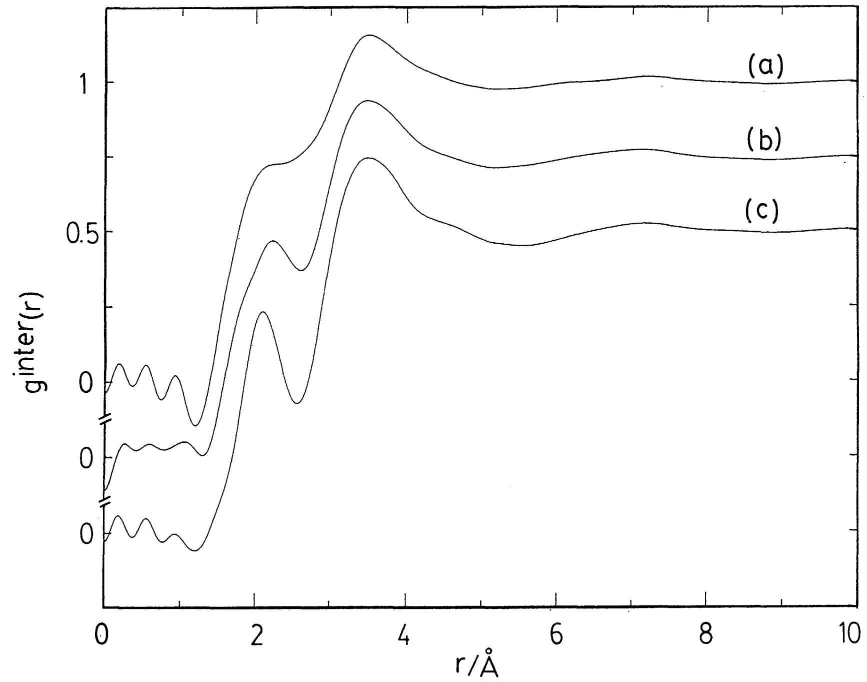

Fig. 6. The intermolecular distribution functions for (a) liquid D_2O, (b) 10 mol% and (c) 23 mol% DCl solutions, respectively.

ing at ca. 2 Å for pure D_2O, corresponding to the nearest neighbor O···D and overlapping D···D correlations, grows to be defined peak centered at ca. 2.1 Å for 23 mol% DCl solution. This peak position is very close to the nearest neighbor Cl^-···D distance found in various solutions which have been examined by the first order difference method using the $^{35}Cl/^{37}Cl$ isotopic substitution.[41] This may be considered to reflect the stability of the first hydration shell around Cl^- in 23 mol% DCl solution.

Triolo and Narten have been reported the existence of the first peak at 1.6 Å in their intermolecular distribution function for $DCl \cdot 3.08D_2O$ solution and have assigned this peak to the nearest neighbor D_3O^+···D distance strongly hydrogen-bonded.[17] There is no clear indication for the resolved peak near 1.6 Å in the present $g^{inter}(r)$ for 23 mol% DCl ($DCl \cdot 3.35D_2O$) solution, although the broad distribution for the nearest neighbor D_3O^+···D pair is suggested in $g^{inter}(r)$. It is at present less clear whether the defined correlation of such pair exists or not in the solution. The inelasticity effect for the $g^{inter}(r)$ itself is generally negligible due to a large effective mass of the molecule.[19] Nevertheless, one of the main causes for the inconsistency between present and previous $g^{inter}(r)$s is considered to be the difference in experimental countermeasure for the inelasticity effect, because the intermolecular term is obtained subtracting the intramolecular term, in which the inelasticity distortion is predominantly significant, from the observed total interference term. At any way, we will hope at near future that the full description of the local structure in the HCl aqueous solution is established by the neutron diffraction experiment involving both the isotopic substitutions for H/D and $^{35}Cl/^{37}Cl$, leading to access the complete set of partial distribution functions.

We wish to acknowledge the help of Dr. Masakatsu Misawa(KENS) and Dr. Toshiharu Fukunaga (Nagoya University) throughout the course of neutron diffraction experiments. All calculations have been performed using ACOS 630 and 3600 computers at the Computing Center of Yamagata University.

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