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X-Ray Diffraction Study of Liquid Water

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The energy-dispersive X-ray diffractometer has been applied to the structural study of liquid water. The intensity data are in good agreement with those obtained by the use of an angle-dispersive method. Water has a structural correlation up to only 8 Å at 25 °C.

By using an energy-dispersive X-ray diffractometer for the determination of the liquid structure, new information was obtained about CCl_4; that is, the existence of fine structures in the diffraction pattern was obtained in the liquid for the first time.[1-3] The fine structures in the diffraction pattern reflect the long-range correlation in the liquid structure. In fact, liquid CCl_4 has a structural correlation up to 28 Å at a low temperature (−20 °C)[3] and even at room temperature.[2] The long-range correlation can be expected to exist also in liquid water, since the molecular interaction of water is a strong hydrogen bond. Therefore, it seems that it is interesting to study the diffraction pattern of water by the energy-distersive method.

At the same time, it is necessary to examine the analytical procedures of the energy-dispersive method. Some difficulties arise for the analysis of the data obtained by this method. One is the consistency of the data which were observed at different scattering angles in the overlapping region, and the other is the absorption correction. The errors caused by the difficulties mentioned above influence the intensity curve in the form of the spurious background and the discontinuity of the curve at the connected points. In this case, the radial distribution curve has ghost peaks. Therefore, it is important to compare our data obtained by the energy-dispersive method with good data obtained by the angle-dispersive method. In 1967, Narten, Danford, and Levy published their results obtained by the X-ray diffraction study of liquid water in the temperature range 4—200 °C.[4] Thereafter they published other related results.[5-7] Though the radial distribution function was also confirmed by other groups,[8-12] the work of Narten *et al.* is regarded as most precise results. It seems, therefore, that it is suitable to compare our data and the results of Narten *et al.*

Another judgement of the correctness of the data analysis can be made by a comparison of the absolute total coherent intensity at $s=0$ with the value calculated from the isothermal compressibility. Moreover, Chonacky and Beeman measured the absolute scattering intensity for water at small scattering angles.[13] This value can also be compared with our data.

Experimental

The scattering intensity of X-rays from liquid water was measured at 25 °C. An energy-dispersive diffractometer[1] with a vertical goniometer (θ—2θ scanning system) was used. A fine-focus X-ray tube with a tungsten target was used at 45 kV, 20 mA. The scattering intensity was recorded by a Si(Li) detector connected with a multi-channel pulse-height analyzer.

The scattering intensity was measured by the transmission method at the scattering angles(2θ) of 2, 4, 8, 12, 17, and 27°. The reflection method was applied at $2\theta=35$ and 70°. By using white X-rays with wavelengths ranging from 0.46 to 1 Å, these measurements cover the ranges of s ($4\pi \sin\theta/\lambda$, λ: wavelength) =0.22—0.48, 0.44—0.96, 0.88—1.92, 1.31—2.88, 1.85—4.07, 2.93—6.43, 3.78—8.29, and 7.20—16.00 Å^{-1} respectively. In order to avoid mistakes in the data analysis for the energy-dispersive method, the scattering angles were set so closely that the two ends of the intensity curves obtained at adjacent angles could overlap widely with each other.

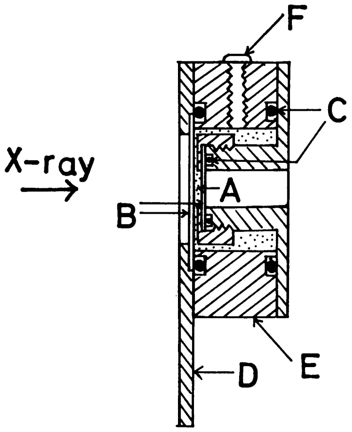

Fig. 1. A modified sample holder for the transmission method. (A): Sample, (B): Be or Myler window, (C): O-ring, (D): stainless steel plate to set the holder to the goniometer, (E): ring (The thickness of the sample can be changed by the exchange of this ring.), (F): the hole from which the sample is injected.

The sample holder used for the reflection method was the same as that used previously.[1] For the transmission method, the sample holder used in our earlier experiment was modified as shown in Fig. 1 in order to set the Be or Myler windows (B) tight and parallel to a narrow spacing. In the present study, Myler film (20 μm thick) was used; the thickness of the sample was 0.194 cm. The scattering intensity was measured for 3×10^4—10^5 s at each scattering angle, and more than 1×10^4 counts per channel were collected.

The scattering intensities from the Myler film of the sample holder and that from air, I_w, were measured, the magnitude of I_w being about 5—8% of the total scattering intensity.

Data Analysis

After smoothing, each scattering intensity curve from which the intensity, I_w, was subtracted was divided by the energy distribution curve of the incident beam (normalization).

As the linear absorption coefficient, μ, changes with the energy of the X-rays, the μ values were calculated in a way similar to that described in a previous paper,[1] in which the C parameters for oxygen and hydrogen atoms were 3.18 and 0.0127 respectively, and in which the D's were 0.0654 and 0.466×10^{-5}.[14] The values of μ, determined from the transmittance of the sample at $\theta=0°$, agree well with the calculated values in the range of wavelengths of 0.46—1 Å within the experimental error. By using the calculated values of the absorption coefficient, the normalized scattering intensity curve were corrected over the wavelength range from 0.46 to 1 Å.

The corrected intensity curve were then converted into the absolute scale (in electron units) by fitting the experimental intensity to the theoretical intensity at large s-values. In the calculation of the theoretical intensity, the internuclear distances and the mean-square amplitudes of the vibration in a water molecule obtained by gas-electron diffraction[15] were used, and the Compton scattering intensity calculated by Cromer[16] was employed. The conversion factor from the experimental to the absolute intensity, K, was easily obtained from $2\theta=2$, 4, 8, 12, and 17°; each intensity curve was successively connected with that at $2\theta=27°$ after the absorption correction. Then, K was obtained for each intensity curve. The observed total coherent intensity;

$$I_{co}(s) = \sum_n f_n(s)^2 + i_1(s) + i_2(s) \qquad (1)$$

is shown in Fig. 2, where $f_n(s)$ is the atomic scattering factor and where $i_1(s)$ and $i_2(s)$ represent the coherent intensities from atom pairs within a molecule and between different molecules respectively. The weighted structure function, $si(s)=s(i_1(s)+i_2(s))$, shown in Fig. 3, was then calculated.

The electronic radial distribution function from which the bulk density was subtracted, $4\pi r^2(\rho-\rho_0)$, was obtained by the Fourier transformation of $si(s)$:

$$4\pi r^2(\rho-\rho_0) = \frac{2r}{\pi\sum_n Z_n^2}\sum_{s=0}^{s_{max}} si(s)\cdot\sin sr\cdot\Delta s, \qquad (2)$$

where ρ_0 is the bulk liquid density and where Z_n is the atomic number of the n-th atom. The electronic radial distribution function is shown in Fig. 4.

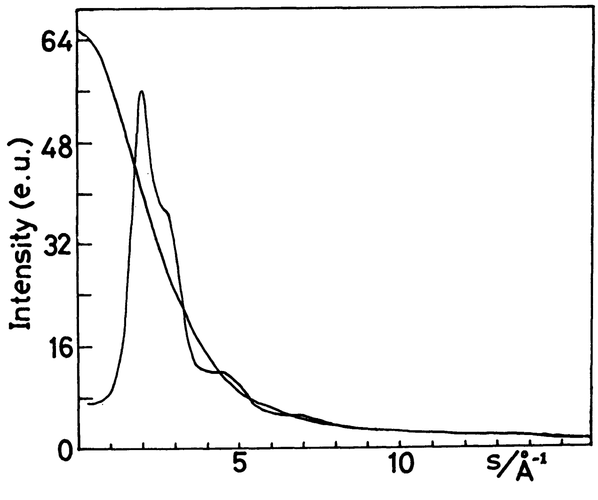

Fig. 2. Observed total coherent intensity I_{CO} for liquid water at 25 °C and independent atomic scattering intensity.

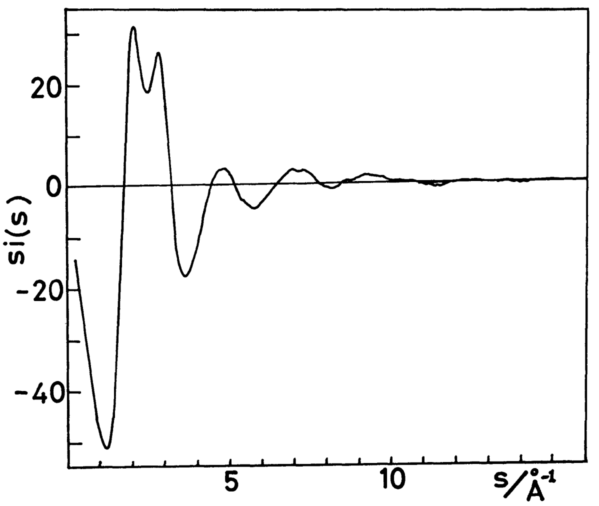

Fig. 3. Weighted structure function $si(s)$ for liquid water at 25 °C.

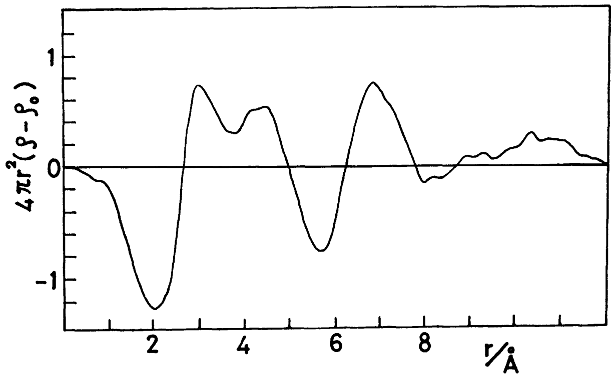

Fig. 4. Electronic radial distribution function from which the bulk density was subtracted, $4\pi r^2(\rho-\rho_0)$.

Results and Discussion

First, we examined to see whether or not the processing of the data obtained by the energy-dispersive method is adequate. In order to show the connection between several intensity data measured at different angles, the raw-intensity-data sets corrected for absorption are plotted in Fig. 5. The data in the $s>6$ Å^{-1} region are not shown in this figure because, in this region, the intensities are almost equal to the self-scattering ones from the corresponding atoms. In each set, the intensity at the extreme of the higher-energy region falls down slightly. In this region, the calculated values of the linear absorption coefficient, μ, are slightly smaller than the observed ones. Except for this, the intensities of the overlapped regions observed at different angles are in good agreement.

It was also confirmed that there was no spurious background which might be caused by inadequate data processing or apparatus functions. Figure 6 shows the weighted structure function, $si(s)$, which was observed

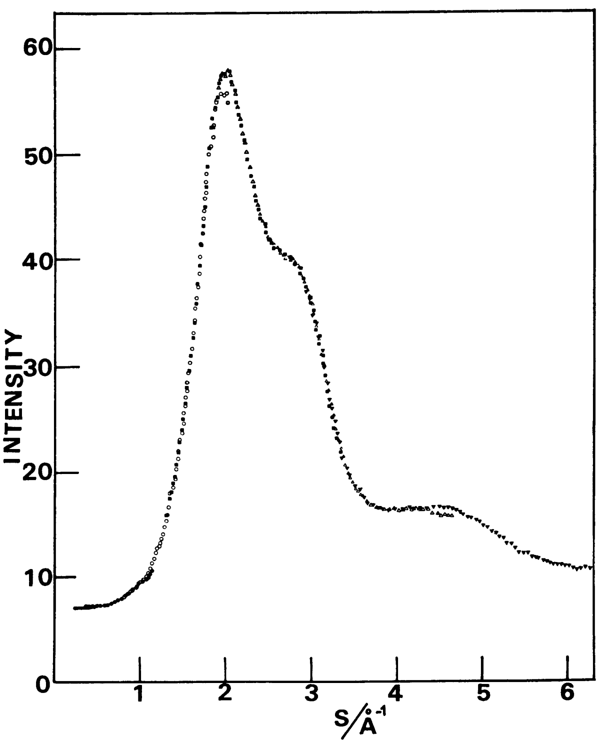

Fig. 5. The raw intensity data of liquid water after absorption correction. Each sign such as ——, ●, ○, ■, △, and ▼ shows the data obtained by angle-setting at $2\theta=2$, 4, 8, 12, 17, and 27° respectively.

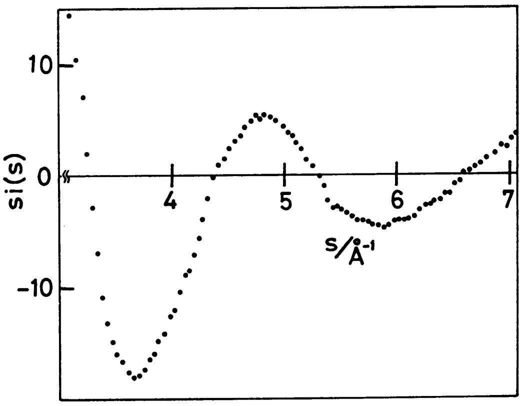

Fig. 6. The weighted structure function $si(s)$, obtained by angle setting at $2\theta=27°$. This result shows that the data do not contain apparatus functions.

at the scattering angle $2\theta=27°$. This curve was obtained as follows. In the case of water, the $i_2=0$ approximation is valid in the $s>6$ Å^{-1} region. Therefore, the data at $2\theta=27°$ could be converted into the absolute scale by adjusting the experimental intensity to the calculated intensity. If the data analysis were not correct, or if the apparatus function were contained in the data, the $si(s)$ curve would ride on a background curve and would never oscillate around the zero line as is shown in Fig. 6.

Second, the above-mentioned data obtained by the energy-dispersive method were compared with those of Narten and Levy[7] measured by the angle-dispersive method. The intensity data of the present work were, therefore, expressed in the form of $H_M(s)$. $H_M(s)$, the structure function whose Fourier transformation gives molecular-pair correlation, is difined as follows:

$$H_M(s) = [I(s)-\langle F^2\rangle]/\langle F\rangle^2. \tag{3}$$

$I(s)$ is the total coherent intensity from the liquid and $<F^2>$ is scattered intensity from one molecule and is given by:

$$\langle F^2\rangle = \sum_i\sum_j f_i(s)f_j(s)\frac{\sin sr_{ij}}{sr_{ij}}\exp\left(-\frac{l_{ij}^2}{2}s^2\right), \tag{4}$$

where l_{ij} denotes the root mean-square amplitude of the vibration around the mean internuclear distance, r_{ij}, $<F>$ is defined by:

$$\langle F\rangle = \sum_i f_i(s)\frac{\sin sr_i}{sr_i}\exp\left(-\frac{l_i^2}{2}s^2\right), \tag{5}$$

where r_j is the distance from the scattering center to the i-th atom. The results are listed in Table 1, with the values obtained by Narten and Levy at 25 °C. The two set of data are in good agreement with each other within 5—6% differences in the range where the intensity curve is gentle. However, a large derivation in the value of $H_M(s)$ is observed at a peak or valley in the intensity curve, for example, at the first peak at nearly $s=2.0$ Å^{-1}. It seems that this deviation is caused by an experimental error in the determination of the s-value. This determination error is within 0.02 Å^{-1} in the s-value, which corresponds to 0.05° angle-setting error for the peak at $s=2.0$ Å^{-1}. From these considerations, it may be concluded that the energy-dispersive data are in good agreement with Narten's data, within the limits of experimental error.

Finally, we have used the absolute total coherent intensity at $s=0$, $I(0)$, for judging the correctness of the data processing. $I(0)$ is related to the isothermal compressibility, κ, as follows:[17]

$$I(0)/(\sum_n Z_n)^2 = \kappa\rho_0 kT \tag{6}$$

where k is the Boltzmann constant and T the absolute temperature. The observed $I(0)$ (7.0 e.u.) does not differ significantly from the value (6.3 e.u.) calculated from Eq. 6 by the use of the reported κ-value (45.7×10^{-12} cm^2 dyn^{-1}, at 25 °C),[18] and it is also almost the same as that obtained by Chonacky and Beeman.[13]

Reproducible fine structures could not be found in the diffraction pattern of liquid water (Fig. 3). As a result of the Fourier transformation of the weighted structure function, the correlation was observed only up to 8 Å. This distance is very short compared with that in CCl_4 (28 Å).[2,3] The finding that the long-range correlation does not exist in liquid water can be interpreted as follows. A water molecule is well arranged among its neighbors according to the strong hydrogen bond, so the structure of liquid water is very bulky. This bulkiness helps to enhance the disorder of the liquid structure. This fact is supported by the density fluctuation obtained by the scattering intensity at small s-values. The observed $I_{CO}(0)$ was obtained by extrapolating the absolute total coherent intensity at small s-values and became 7.0 e.u. (electron units). This value shows that one water molecule fluctuates in a

Table 1. The comparison of the structure functions for liquid water

s	$H_M(s)$		s	$H_M(s)$		s	$H_M(s)$		s	$H_M(s)$	
	Narten	This work		Narten	This work		Narten	This work		Narten	This work
0.00	−0.938	−0.930	0.08	−0.938	−0.930	8.16	−0.054	−0.052	8.24	−0.054	−0.053
0.16	−0.938	−0.930	0.24	−0.937	−0.930	8.32	−0.050	−0.049	8.40	−0.042	−0.040
0.32	−0.937	−0.929	0.40	−0.936	−0.929	8.48	−0.033	−0.030	8.56	−0.023	−0.024
0.48	−0.935	−0.928	0.56	−0.932	−0.928	8.64	−0.013	−0.009	8.72	−0.005	−0.004
0.64	−0.928	−0.924	0.72	−0.921	−0.920	8.80	0.003	0.002	8.88	0.010	0.009
0.80	−0.913	−0.916	0.88	−0.902	−0.906	8.96	0.017	0.018	9.04	0.023	0.025
0.96	−0.890	−0.899	1.04	−0.878	−0.888	9.12	0.028	0.027	9.20	0.031	0.033
1.12	−0.861	−0.872	1.20	−0.835	−0.846	9.28	0.032	0.030	9.36	0.031	0.029
1.28	−0.796	−0.815	1.36	−0.748	−0.770	9.44	0.029	0.029	9.52	0.027	0.024
1.44	−0.685	−0.704	1.52	−0.599	−0.622	9.60	0.025	0.023	9.68	0.021	0.019
1.60	−0.478	−0.507	1.68	−0.320	−0.371	9.76	0.015	0.017	9.84	0.007	0.010
1.76	−0.158	−0.216	1.84	−0.002	−0.039	9.92	−0.001	0.002	10.00	−0.009	−0.006
1.92	0.119	0.080	2.00	0.190	0.169	10.08	−0.014	−0.014	10.16	−0.017	−0.014
2.08	0.212	0.192	2.16	0.157	0.194	10.24	−0.018	−0.013	10.32	−0.019	−0.015
2.24	0.166	0.165	2.32	0.134	0.142	10.40	−0.020	−0.015	10.48	−0.020	−0.016
2.40	0.116	0.124	2.48	0.119	0.130	10.56	−0.020	−0.016	10.64	−0.019	−0.018
2.56	0.147	0.147	2.64	0.193	0.169	10.72	−0.016	−0.015	10.80	−0.012	−0.014
2.72	0.245	0.220	2.80	0.287	0.268	10.88	−0.009	−0.010	10.96	−0.007	−0.008
2.88	0.301	0.293	2.96	0.277	0.286	11.04	−0.005	−0.007	11.12	−0.003	−0.005
3.04	0.215	0.256	3.12	0.125	0.171	11.20	0.000	−0.003	11.28	0.003	0.002
3.20	0.022	0.073	3.28	−0.079	−0.027	11.36	0.007	0.006	11.44	0.010	0.009
3.36	−0.164	−0.119	3.44	−0.227	−0.187	11.52	0.013	0.011	11.60	0.016	0.017
3.52	−0.262	−0.232	3.60	−0.271	−0.251	11.68	0.017	0.016	11.76	0.017	0.017
3.68	−0.255	−0.356	3.76	−0.233	−0.245	11.84	0.015	0.016	11.92	0.013	0.014
3.84	−0.199	−0.230	3.92	−0.205	−0.200	12.00	0.010	0.013	12.08	0.008	0.010
4.00	−0.124	−0.171	4.08	−0.083	−0.106	12.16	0.006	0.011	12.24	0.003	0.005
4.16	−0.039	−0.060	4.24	0.005	−0.005	12.32	0.000	0.001	12.40	−0.002	0.001
4.32	0.045	0.030	4.40	0.076	0.074	12.48	−0.004	−0.002	12.56	−0.005	−0.004
4.48	0.098	0.088	4.56	0.114	0.100	12.64	−0.005	−0.006	12.72	−0.006	−0.006
4.64	0.126	0.115	4.72	0.135	0.126	12.80	−0.007	−0.005	12.88	−0.010	−0.008
4.80	0.140	0.125	4.88	0.136	0.120	12.96	−0.012	−0.009	13.04	−0.011	−0.012
4.96	0.124	0.118	5.04	0.104	0.096	13.12	−0.009	−0.010	13.20	−0.006	−0.007
5.12	0.080	0.079	5.20	0.057	0.053	13.28	−0.003	−0.005	13.36	−0.001	−0.004
5.28	0.035	0.020	5.36	0.013	−0.005	13.44	0.001	−0.001	13.52	0.002	0.000
5.44	−0.009	−0.015	5.52	−0.034	−0.039	13.60	0.005	0.003	13.68	0.007	0.005
5.60	−0.057	−0.063	5.68	−0.078	−0.078	13.76	0.008	0.007	13.84	0.008	0.009
5.76	−0.093	−0.100	5.84	−0.102	−0.108	13.92	0.007	0.008	14.00	0.005	0.007
5.92	−0.105	−0.099	6.00	−0.102	−0.093	14.08	0.004	0.007	14.16	0.004	0.005
6.08	−0.094	−0.088	6.16	−0.080	−0.078	14.24	0.004	0.006	14.32	0.004	0.005
6.24	−0.063	−0.060	6.32	−0.044	−0.045	14.40	0.002	0.004	14.48	0.000	0.002
6.40	−0.026	−0.029	6.48	−0.009	−0.011	14.56	−0.002	0.001	14.64	−0.003	−0.002
6.56	0.007	0.017	6.64	0.023	0.029	14.72	−0.004	−0.003	14.80	−0.004	−0.004
6.74	0.040	0.039	6.80	0.056	0.059	14.88	−0.004	−0.005	14.96	−0.004	−0.005
6.88	0.069	0.070	6.96	0.075	0.087	15.04	−0.004	−0.003	15.12	−0.003	−0.003
7.04	0.077	0.089	7.12	0.074	0.080	15.20	−0.003	−0.002	15.28	−0.003	−0.002
7.20	0.069	0.070	7.28	0.063	0.065	15.36	−0.003	−0.001	15.44	−0.003	−0.001
7.36	0.053	0.055	7.44	0.040	0.047	15.52	−0.002	0.000	15.60	−0.001	0.000
7.52	0.024	0.023	7.60	0.007	0.010	15.68	0.000	0.000	15.76	0.000	0.000
7.68	−0.008	−0.005	7.76	−0.020	−0.018	15.84	−0.001	0.000	15.92	−0.002	0.000
7.84	−0.030	−0.025	7.92	−0.039	−0.035	16.00	−0.003	0.000			
8.00	−0.044	−0.040	8.08	−0.050	−0.048						

volume of 467 Å^3. In other word, since 15.6 water molecules are contained in this volume, there are 15.6±1 molecules in 467 Å^3 for water at room temperature. On the other hand, there are 63±1 molecules in 1.00×10^4 Å^3 for liquid CCl_4.1)

There are many models for the structure of liquid water,19) and an effort to obtain the atom-atom pair correlation functions, that is $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$ has been made experimentally.20,21) However, our search for a satisfactory model of liquid water must be left for future study.

In conclusion, it was ascertained that the analysis for the energy-dispersive method was appropriate, and that data obtained by the use of energy-dispersive method were in good agreement with Narten's results within the limits of experimental error. It seems that in the present experiment the energy-dispersive method was given a sound basis for further application to more different systems.

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