Bull. Chem. Soc. Jpn., 57, 329—333 (1984)

# The Structure of Liquid Water by Neutron Scattering. III. Calculations of the Partial Structure Factors

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(Received June 8, 1983)

A formula for obtaining partial structure factors for fluid systems composed of molecular clusters with various sizes was derived according to the theoretical procedure proposed in the preceding papers (N. Ohtomo, K. Tokiwano, and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **54**, 1802 (1981): **55**, 2788 (1982)). The formula was applied to calculate partial structure factors of liquid water, and from the good agreement between the calculated and observed values the pentamer-monomer mixture model for liquid water was confirmed as reasonable.

As the result of neutron diffraction studies of liquid water reported in the preceding papers,[1,2)][††] the pentamer–monomer mixture model turned out to be the best structure model of water, where the total neutron structure factors obtained were interpreted successfully by that model.

Quite recently, two partial structure factor data of liquid water at 25 °C were reported by Thiessen and Narten[3)] and by Soper and Silver[4)] using an isotope substitution technique of neutron diffraction. A comparison between calculated and observed partial structure factors will offer a very sensitive test for the structure model of liquid. However, no useful theoretical procedure has been proposed for the calculation of partial structure factors for associated liquids like water.

In the present study, thus, we attempt to derive a formula useful for obtaining partial structure factors for the fluid system composed of molecular clusters with various sizes based on the theoretical procedure proposed in paper I and II.[1,2)] Then the partial structure factors of liquid water for the pentamer–monomer mixture model are calculated by the use of the formula derived, and the results are compared with the observed data.[3,4)]

## Procedure of Calculations of Partial Structure Factors

*Partial Structure Factors for Fluids Composed of Molecular Clusters.* For a $r$-component system, the partial structure factors $S_{ss'}(Q)$ are connected with the total structure factor $S_m(Q)$ by

$$S_m(Q) = \Sigma^{-2}\sum_{s,s'}^{r} c_s c_{s'} b_s b_{s'} S_{ss'}(Q), \tag{1}$$

where $\Sigma \equiv \sum_{s}^{r} c_s b_s$, $b_s$ the coherent scattering length for the nucleus species s, $c_s$ the number of the nuclei per molecular unit, and $Q \equiv |\vec{Q}|$ ($\vec{Q}$: the scattering vector).

We consider here the case of a fluid system consisting of molecular clusters with various sizes including monomers and, then, begin with Eq. 12 for $S_m(Q)$ in paper II,

$$S_m(Q) = \sum_{\nu}\frac{x_\nu}{\nu} f_1^\nu(Q) + \sum_{\nu \geqq 2}\frac{x_\nu}{\nu} f_c^\nu(Q) + \bar{f}_{2U}(Q)[S_c(Q) - 1], \tag{2}$$

where $x_\nu$ is the fraction of $\nu$-mer clusters in molecular number, the $f_1^\nu(Q)$ the intramolecular contribution within the clusters (Eq. 13 in II), $f_c^\nu(Q)$ the factor originating from the orientational correlation of molecules within the clusters (Eq. 14 in II), $S_c(Q)$ the molecular-centers structure factor of the liquid (Eq. 10 in II), and $\bar{f}_{2U}(Q)$ an extended form of a factor resulting from the completely uncorrelated orientational configuration between molecules in the liquid (Eq. 11 in II). We rewrite $f_c^\nu(Q)$ as

$$f_c^\nu(Q) = \nu f_1^c(Q) - f_1^\nu(Q) - \nu f_3^\nu(Q) \cdot f_{2U}^\nu(Q), \tag{3}$$

where

$$f_1^c(Q) = \Sigma^{-2}\frac{1}{\nu}[< \sum_{l,l'}\sum_{n_l,n_{l'}} b_{n_l} b_{n_{l'}} \exp(i\vec{Q}\cdot\vec{r}_{n_l n_{l'}}) >]_\nu, \tag{4}$$

$$f_3^\nu(Q) = \frac{1}{\nu}[< \sum_{l \neq l'} \exp(i\vec{Q}\cdot\vec{r}_{cll'}) >]_\nu \quad (\nu \geqq 2), \tag{5}$$

and

$$f_{2U}^\nu(Q) = \Sigma^{-2}\frac{1}{\nu}[\sum_{l}^{\nu}[\sum_{n_l} b_{n_l} < \exp(i\vec{Q}\cdot\vec{r}_{cn_l}) >]^2]_\nu. \tag{6}$$

Suffix $l$ denotes the $l$-th molecule within the $\nu$-mer cluster and $n_l$ the n-th nucleus in the molecule $l$. $\vec{r}_{n_l n_{l'}}$ is the vector distance from the $n_l$-th nucleus to the $n_{l'}$-th one, $\vec{r}_{cll'}$ the vector distance from the center of the $l$-th molecule to that of the $l'$-th one, and $\vec{r}_{cn_l}$ the vector distance from the center of the molecule $l$ to its $n_l$-th nucleus, within the $\nu$-mer cluster. $f_1^c(Q)$ is the contribution of atom-pairs within the $\nu$-mer cluster (Eq. 8 in I), $f_3^\nu(Q)$ a factor resulting from the molecular-center pairs within the cluster (Eq. 11 in I), and $f_{2U}^\nu(Q)$ an extended form of a factor resulting from the completely-uncorrelated orientational configuration between molecules within the cluster.

Introducing Eq. 3 into Eq. 2, we obtain

$$S_m(Q) = \sum_{\nu} x_\nu \left[\frac{1}{\nu} f_1^\nu(Q)\delta_{\nu 1} + f_1^c(Q)(1 - \delta_{\nu 1}) - f_3^\nu(Q) \cdot f_{2U}^\nu(Q)\right] + \bar{f}_{2U}(Q)[S_c(Q) - 1], \tag{7}$$

where $\delta_{ik}$ is Kronecker's $\delta$.

From Eqs. 1 and 7, we can obtain the partial structure factors $S_{ss'}(Q)$ for the liquid composed of molecular clusters of various sizes including monomers. The Eq. 1 has a quadratic form on $b_s$ as well as the Eq. 7, though in Eq. 7 the $b_s$ are contained in an implicit form. And then, we can obtain the formula of $S_{ss'}(Q)$ by comparing these two equations, when an explicit form of the total $S_m(Q)$ is given. Thus, the formula of $S_{ss'}(Q)$ is obtained for the practical model of the liquid under consid-

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[††] We cite Refs. 1 and 2 as paper I and II, respectively, in the following.

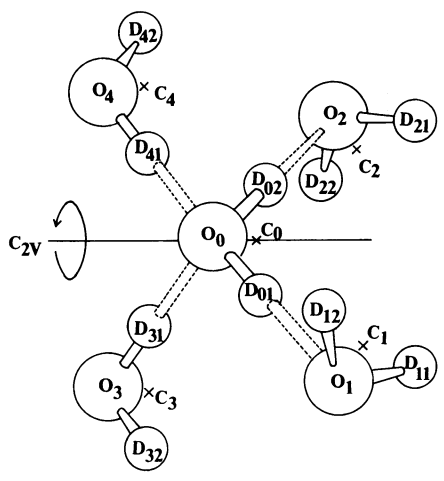

Fig. 1. The structure of the regular tetrahedral pentamer with the C2v symmetrical coordination. The suffix $O_i$ indicates oxygen in the $i$-th molecule within the pentamer, $D_{ij}$ the $j$-th deuteron in the $i$-th molecule, and $C_i$ the molecular center of the $i$-th molecule.

eration.

*Partial Structure Factors for Pentamer–Monomer Mixture Model.* For liquid water, using three partial structure factors $S_{OO}(Q)$, $S_{OD}(Q)$, and $S_{DD}(Q)$, Eq. 1 becomes

$$S_m(Q) = \Sigma^{-2}[b_O{}^2 S_{OO}(Q) + 4b_O b_D S_{OD}(Q) + 4\, b_D{}^2 S_{DD}(Q)], \tag{8}$$

where $\Sigma = b_O + 2b_D$.

In order to calculate the partial structure factors, we adopt the pentamer–monomer mixture model fully examined in paper II, which is composed of regular tetrahedral pentamers with the C2v symmetrical coordination (Fig. 1) and monomers as its constituents. In this case, we put $x_1 \neq 0$ and $x_5 \neq 0$ (others=zero). Since $\bar{f}_{2U}(Q) = x_1 f_{2U}^1(Q) + x_5 f_{2U}^5(Q)$, Eq. 7 becomes

$$S_m(Q) = x_1\{f_1^1(Q) + f_{2U}^1(Q)[S_c(Q) - 1]\} + x_5\{S_m^p(Q) + f_{2U}^5(Q)[S_c(Q) - f_3^5(Q) - 1]\}. \tag{9}$$

The intra-pentamer contribution $S_m^p(Q)$ ($\equiv f_1^c(Q)$ for pentamer) is given from Eq. 13 in paper I as

$$S_m^p(Q) = \frac{1}{5} f_1^5(Q) + \Sigma^{-2}[b_O{}^2 S_{m,p}^{(OO)}(Q) + 4b_O b_D S_{m,p}^{(OD)}(Q) + 4b_D{}^2 S_{m,p}^{(DD)}(Q)]. \tag{10}$$

The factors $S_{m,p}^{(OO)}(Q)$, $S_{m,p}^{(OD)}(Q)$, and $S_{m,p}^{(DD)}(Q)$, are the intra-pentamer part of the contributions of the O–O, O–D, and D–D pairs, respectively, and the explicit expressions are written below when the orientational configuration of water molecules within the pentamer is specified. The intramolecular contribution $(1/\nu) f_1^\nu(Q)$ ($\nu=1$ for monomer and $\nu=5$ for pentamer) is

$$\frac{1}{\nu} f_1^\nu(Q) = \Sigma^{-2}[b_O{}^2 + 2b_D{}^2 + 4b_O b_D Y_{OD}^\nu(Q) + 2b_D{}^2 Y_{DD}^\nu(Q)], \tag{11}$$

and

$$Y_{nn'}^\nu(Q) = j_0(Q r_{nn'}^\nu) \exp(-\gamma_{nn'}^\nu Q^2), \tag{12}$$

where $j_0(x) = \sin x/x$, $r_{nn'}^\nu$ is the distance between two different nuclei n and n′ within a molecule and $2\gamma_{nn'}^\nu$ the mean-square variation to the distance $r_{nn'}^\nu$. The factor $f_{2U}^\nu(Q)$ is

$$f_{2U}^\nu(Q) = \Sigma^{-2}[b_O{}^2\{Y_{cO}^\nu(Q)\}^2 + 4b_O b_D Y_{cO}^\nu(Q) Y_{cD}^\nu(Q) + 4b_D{}^2\{Y_{cD}^\nu(Q)\}^2], \tag{13}$$

where the suffix c denotes the molecular center.

From Eqs. 8—13, the partial structure factors $S_{OO}(Q)$, $S_{OD}(Q)$, and $S_{DD}(Q)$ for liquid water are given explicitly as follows:

$$S_{OO}(Q) = x_1[1 + \{Y_{cO}^1(Q)\}^2[S_c(Q) - 1]] + x_5[1 + S_{m.p}^{(OO)}(Q) + \{Y_{cO}^5(Q)\}^2[S_c(Q) - f_3^5(Q) - 1]], \tag{14}$$

$$S_{OD}(Q) = x_1[Y_{OD}^1(Q) + Y_{cO}^1(Q) Y_{cD}^1(Q)[S_c(Q) - 1]] + x_5[Y_{OD}^5(Q) + S_{m,p}^{(OD)}(Q) + Y_{cO}^5(Q) Y_{CD}^5(Q)[S_c(Q) - f_3^5(Q) - 1]], \tag{15}$$

and

$$S_{DD}(Q) = x_1\left[\frac{1}{2}\{1 + Y_{DD}^1(Q)\} + \{Y_{cD}^1(Q)\}^2[S_c(Q) - 1]\right] + x_5\left[\frac{1}{2}\{1 + Y_{DD}^5(Q)\} + S_{m.p}^{(DD)}(Q) + \{Y_{cD}^5(Q)\}^2[S_c(Q) - f_3^5(Q) - 1]\right]. \tag{16}$$

For the C2v symmetry pentamer (Fig. 1), $S_{m,p}^{(OO)}(Q)$, $S_{m,p}^{(OD)}(Q)$, and $S_{m,p}^{(DD)}(Q)$ are given as Eqs. 16, 17, and 18 in I, respectively, and the factor $f_3^5(Q)$ is

$$f_3^5(Q) = \frac{1}{5}[8Y_{c_0c_1}(Q) + 4\{Y_{c_1c_3}(Q) + Y_{c_1c_4}(Q)\} + 2\{Y_{c_1c_2}(Q) + Y_{c_3c_4}(Q)\}]. \tag{17}$$

For the $S_c(Q)$ required in the calculation of Eqs. 14—16, we can use the observed X-ray intensity data, considering from the fact that the first peak mainly expresses the averaged packing of water molecules in the liquid.

*Parameters Used in the Present Calculation.* According to the procedure described above, we can calculate the $S_{OO}(Q)$, $S_{OD}(Q)$, and $S_{DD}(Q)$ for the pentamer–monomer mixture model with an appropriate value of pentamer fraction $x_5$ and other several parameters (intramolecular distances, distances between molecular centers, mean-square variations, *etc*). The calculated curves are compared with the experimental data at 25 °C by Thiessen and Narten[3] and by Soper and Silver.[4]

According to the result in paper II the value of $x_5$ is 0.85 at 25 °C. Then, we use $x_1 = 0.15$ and $x_5 = 0.85$ in the present analysis.

The values of molecular parameters are identical with those in paper II: for pentamer, $r_{OD}^5 = 0.98$ Å, $r_{DD}^5 = 1.60$ Å, and DOD angle=109.5° corresponding to the molecule in heavy ice-I, for monomer, $r_{OD}^1 = 0.96$ Å, $r_{DD}^1 = 1.52$ Å, and DOD angle=104.5° corresponding to the molecule in the vapor, and for the hydrogen-bonding, $r_{O_1O_2}$ (=$r_{OO}$ in paper II)=2.85 Å and the O-O-O angle=109.5°.

In performing calculations, the determination of molecular centers is required and there are three ways of defining the molecular center: the center of mass of the molecule $\vec{r}_G$, the definition as $\vec{r}_{c1}=\Sigma b_n\vec{r}_n/\Sigma b_n$,[6] and

$$\vec{r}_{c_2} = \frac{\sum b_n{}^2\vec{r}_n}{\sum b_n{}^2}, \tag{18}$$

where n ranges over the nuclei in a molecule. Positions of the three types of molecular center in heavy water molecules ($b_O=0.58\times10^{-12}$ cm and $b_D=0.67\times10^{-12}$ cm)[7] are indicated in Fig. 2. As seen in the figure, $\vec{r}_{c1}\simeq\vec{r}_{c2}$ for heavy water molecule. Thus, we adopt here the two kinds of molecular centers, $\vec{r}_G$, and $\vec{r}_{c2}$.

With respect to the magnitudes of Debye-Waller factors, assuming the mean-square variation $2\gamma^{\nu}_{nn'}\propto$ the inter-nucleus distance $r^{\nu}_{nn'}$,[8] we assign the following values to the rms variation $\{2\gamma^{\nu}_{nn'}\}^{1/2}$ as: first, $D_1=0.06$ Å$^{1/2}$ per 1 Å for intramolecular distances ($r^1_{OD}$, $r^1_{DD}$, $r^5_{OD}$, $r^5_{DD}$, $r^1_{cO}$, $r^1_{cD}$, $r^5_{cO}$, and $r^5_{cD}$) and for hydrogen-bonded distances ($r_{O_0O_1}$, and $r_{O_1D_{01}}$); second, $D_2=0.07$ Å$^{1/2}$ per 1 Å for the seven intermolecular distances ($r_{O_1O_2}$, $r_{O_0D_{11}}$, $r_{O_1D_{31}}$, $r_{D_{01}D_{11}}$, $r_{D_{01}D_{21}}$, $r_{D_{01}D_{22}}$, and $r_{D_{31}D_{41}}$) and for five distances between molecular centers ($r_{c_0c_1}$, $r_{c_1c_2}$, $r_{c_1c_3}$, $r_{c_1c_4}$, and $r_{c_3c_4}$); third, $D_3=0.1$ Å$^{1/2}$ per 1 Å for four intermolecular (distances ($r_{O_1D_{21}}$, $r_{O_1D_{22}}$, $r_{D_{12}D_{41}}$, and $r_{D_{11}D_{31}}$); and, fourth, $D_4=0.2$ Å$^{1/2}$ per 1 Å for four intermolecular distances ($r_{D_{11}D_{21}}$, $r_{D_{11}D_{22}}$, $r_{D_{11}D_{42}}$, and $r_{D_{12}D_{22}}$).

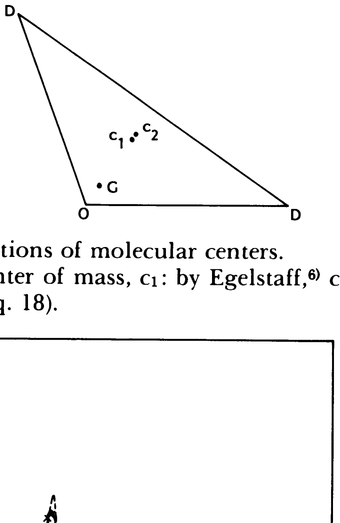

Fig. 2. Positions of molecular centers.
G: The center of mass, c1: by Egelstaff,[6] c2: by the authors (Eq. 18).

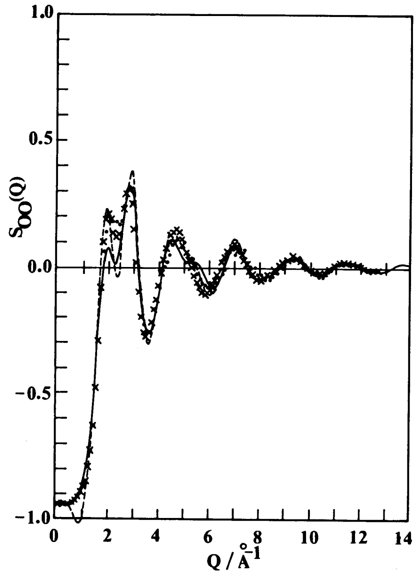

Fig. 3. Comparison between the calculated $S_{OO}(Q)$ for the $C_{2v}$ symmetry model and observed data.
——: $S^{c2}_{OO}(Q)$ calculated, ------: $S^{G}_{OO}(Q)$ calculated, ●: neutron diffraction data by Thiessen and Narten,[3] ×: X-ray dffraction data by Narten.[9]

## Results and Discussion

*Comparison between Calculated Partial Structure Factors $S_{OO}(Q)$, $S_{OD}(Q)$, and $S_{DD}(Q)$ and Observed Data.* Now, we can calculate the $S_{OO}(Q)$, $S_{OD}(Q)$, and $S_{DD}(Q)$, using Eqs. 14—18 together with the observed X-ray intensity data at 25 °C[9] for the $S_c(Q)$. The calculated O-O, O-D, and D-D structure factors are shown in Figs. 3, 4, and 5, respectively, and compared with the corresponding observed data. All calculated curves essentially reproduce the observed data successfully on the whole. Detailed features observed in these figures are described in the following.

Two calculated curves, $S^{c2}_{OO}(Q)$ and $S^{G}_{OO}(Q)$, are indicated in Fig. 3, where upper suffixes c2 and G shows the factor for the case when $\vec{r}_{c_2}$ and $\vec{r}_G$ is taken as the molecular center respectively. The $S^{c2}_{OO}(Q)$ is in agreement with the observed data on the whole, except for the deviation in the first peak at 2.1 Å$^{-1}$ and that near $Q\simeq5$ Å$^{-1}$. On the other hand, an over oscillatory behavior appears in the calculated $S^{G}_{OO}(Q)$ curve, though a good agreement in the first peak. On the whole, the $S^{c2}_{OO}(Q)$ curve is somewhat better than $S^{G}_{OO}(Q)$ and the small difference between $S^{c2}_{OO}(Q)$ and $S^{G}_{OO}(Q)$ is attributed to the different magnitudes of the factors $Y^{c2}_{cO}(Q)$ and $Y^{G}_{cO}(Q)$ mainly.

With respect to the $S_{OD}(Q)$ shown in Fig. 4(a), the main features of the observed data are seen as: the

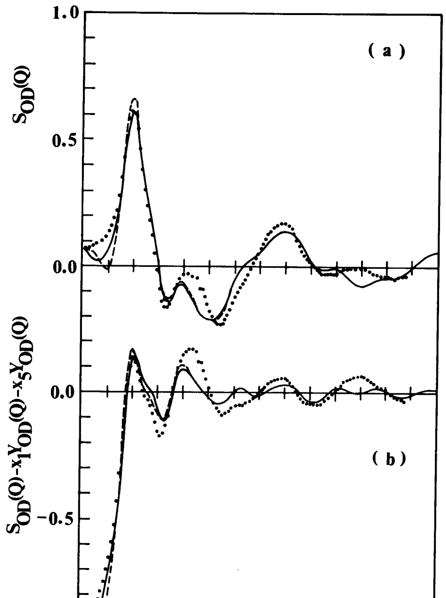

Fig. 4. Comparison between calculated O-D structure factors for the $C_{2v}$ symmetry model and observed data.
(a) $S_{OD}(Q)$ (●: $S_{OD}(Q)$ observed by Thiessen and Narten[3]), (b) $S_{OD}(Q)-x_1Y^1_{OD}(Q)-x_5Y^5_{OD}(Q)$ (●: intermolecular part of $S_{OD}(Q)_{obsd}$ from which the intramolecular contribution of the pentamer-monomer mixture model is subtracted), ——: calculated curves ($\vec{r}_{c_2}$ as the molecular center), ------: calculated curves ($\vec{r}_G$ as the molecular center).

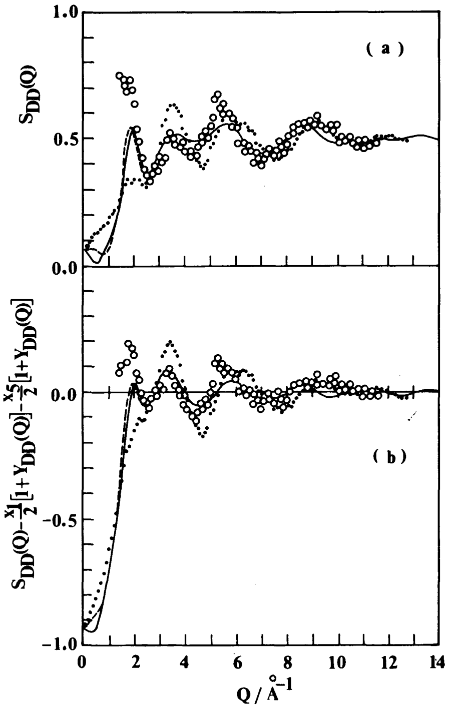

Fig. 5. Comparison between calculated D–D structure factors for the C$_{2v}$ symmetry model and observed data.
(a) $S_{DD}(Q)$ (○: $S_{DD}(Q)$ observed by Soper and Silver,[4) ●: $S_{DD}(Q)$ observed by Thiessen and Narten[3)), (b) $S_{DD}(Q)-\frac{x_1}{2}[1+Y^1_{DD}(Q)]-\frac{x_5}{2}[1+Y^5_{DD}(Q)]$ (○: intermolecular part of $S_{DD}(Q)_{obsd}$ by Soper and Silver[4) from which the intramolecular contribution of the pentamer–monomer mixture model is subtracted, ●: intermolecular part of $S_{DD}(Q)_{obsd}$ by Thiessen and Narten[3) from which the intramolecular contribution of the pentamer–monomer mixture model is subtracted), ——: calculated curves ($\vec{r}_{c2}$ as the molecular center), ------: calculated curves ($\vec{r}_G$ as the molecular center).

largest peak at 2 Å$^{-1}$, a bump at *ca.* 4 Å$^{-1}$ a deep minimum at *ca.* 5 Å$^{-1}$ and a broader peak ranging over 6—9 Å$^{-1}$. The calculated curve essentially reproduces these features of the $S_{OD}(Q)$ data. Especially, the agreement between the $S^{c2}_{OD}(Q)$ and the observed data is excellent in the range of the first peak, 1—3 Å$^{-1}$. A large deviation of the calculated $S^{G}_{OD}(Q)$ curve from the data is seen in the lower $Q$ range, like the case of O–O structure factor (Fig. 3). The same trend is found in the intermolecular part of the O–D structure factor, $S_{OD}(Q)-x_1Y^1_{OD}(Q)-x_5Y^5_{OD}(Q)$, shown in Fig. 4(b).

In Fig. 5, the calculated D–D structure factors are compared with the neutron diffraction data at reactor by Thiessen and Narten[3) and those at LINAC by Soper and Silver.[4) The two recent experimental data agree with each other on the whole. But, several noticeable deviations are observed. Taking account of the experimental difficulties in determining partial structure factors, we can see in Fig. 5(a) that the calculated $S^{c2}_{DD}(Q)$ and $S^{G}_{DD}(Q)$ curves are in essential agreement with Soper and Silver's data on the whole. With respect to these features, the behavior of the intermolecular part of the $S_{DD}(Q)$ shown in Fig. 5(b) is quite similar to that of the $S_{DD}(Q)$ on the whole. Thus, we can state that the pentamer-monomer mixture model with the regular tetrahedral pentamer of the C$_{2v}$ symmetrical structure reproduces the fundamental character of the D–D structure factors satisfactorily. In addition, the appearance of the first peak at 2 Å$^{-1}$ in the calculated curves as well as in Soper and Silver's data is noticeable, though the magnitude of the calculated curves is only half that of their data.

Thus, the agreement between the calculated structure factor curves and observed data suggests the essential effectiveness of the pentamer-monomer mixture model with the regular tetrahedral pentamer as its dominant constituent.

We have taken so far the molecular center to be at the oxygen nucleus, similarly to the choice by Page and Powles,[5) and successfully interpreted the total structure factors of heavy water.[1,2) When the center is taken so, the $S_{OO}(Q)$ is reduced to $S_c(Q)$ resultantly as seen in Eq. 14, and then a reasonable estimation of the molecular center is required for the present calculation. As described in the preceding section, we have adopted two kinds of molecular centers for heavy water molecule, $\vec{r}_{c2}$ and $\vec{r}_G$ (Fig. 2), and have calculated the partial structure factors (Figs. 3—5). The reasonable choice of the molecular center is practically important in obtaining successful results. Moreover, it is pointed out, as a noticeable feature, that the calculated curves are independent on the choice of molecular centers in this work, although only slight deviations of the $S^{G}_{ss'}(Q)$ from $S^{c2}_{ss'}(Q)$ appear in lower $Q$ region as seen in Figs. 3—5.

*Freely Rotating Model.* It is of much interesting whether the overall orientational configuration of water molecules in tetrahedral pentamer is the C$_{2v}$ symmetry or the freely rotating, with respect to peripheral molecules. In paper I, we calculated the total structure factors for the freely rotating model in addition to the C$_{2v}$ symmetry model. In the former model, the peripheral molecules are rotating freely around the axis on a straight line joining the central and peripheral oxygens. Here, we calculate the partial structure factors of the freely rotating model also. Then, for that model, we have assumed that the positions of outer six deuterons are reduced to those of peripheral oxygens on the average and also that the positions of all the molecular centers are reduced to those of oxygens within the molecule including its molecular center. Accordingly, the $S^{(OD)}_{m,p}(Q)$ and $S^{(DD)}_{m,p}(Q)$ are written as

$$S^{(OD)}_{m,p}(Q)=\frac{1}{5}[2Y_{O_1D_{01}}(Q)+3Y_{O_1D_{31}}(Q)+6Y_{O_0D_{11}}(Q)+9Y_{O_1O_2}(Q)], \tag{19}$$

and

$$S^{(DD)}_{m,p}(Q)=\frac{1}{10}[Y_{D_{31}D_{41}}(Q)+8Y_{O_0D_{11}}(Q)+10Y_{O_1D_{31}}(Q)+8Y_{O_1D_{01}}(Q)+13Y_{O_1O_2}(Q)], \tag{20}$$

respectively, and $f^5_3(Q)$ (Eq. 20) is reduced to Eq. 17. Equations 19 and 20 are identical with Eqs. 19 and 20 in paper I, where a typographical error in Eq. 20 in paper I is corrected.[10) Then, for the freely rotating model, using Eqs. 14—20, we calculated the O–O, O–D, and

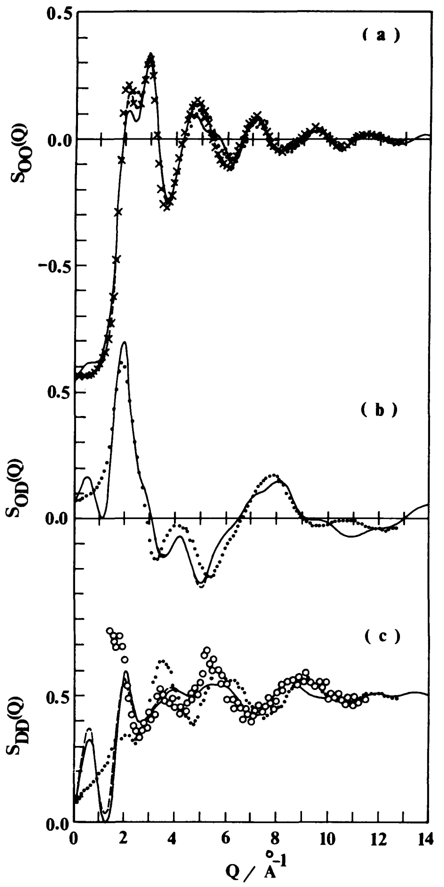

Fig. 6. Comparison between calculated partial structure factors for the freely rotating model and observed data.
○: Neutron diffraction data by Soper and Silver,[4] ●: neutron diffraction data by Thiessen and Narten,[3] ×: X-ray diffraction data by Narten,[9] ——: calculated curves ($\vec{r}_{c_2}$ as the molecular center), -------: calculated curves ($\vec{r}_G$ as the molecular center).

D-D structure factors. The calculated curves are shown in Fig. 6.

Compared Figs. 6(a)—(c) with Figs. 3—5, respectively, it is found that the difference between the results for the freely rotating model and those for the $C_{2v}$ symmetry model is very slight, except the D-D structure factors in lower $Q$ region. As seen in Figs. 5 and 6(c), the calculated $S_{DD}(Q)$ curves for both models are fairly different from each other in lower $Q$ region ($\lesssim 1.5$ Å$^{-1}$). This means the fact that the D-D structure factors in low $Q$ region dominantly reflect the orientational configuration of water molecules in the liquid. Thus, the marked deviation of the calculated $S_{DD}(Q)$ curve for the freely rotating model from the observed data is considered to indicate that the model behaves only as an approximate one.

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10) In paper I the calculations for the freely rotating model were performed by using the right expression Eq. 20 given in this text throughout, and then the curves shown in Figs. 6 and 7 in paper I are correct ones.