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Intramolecular Structure Study of Liquid Methanol by Neutron Diffraction on Electron LINAC

Haruo FUJIMORI*, Takaaki MATSUMOTO*
and Meiseki KATAYAMA*

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Abstract

A structure study of liquid methanol was performed by means of neutron diffraction using a 45 MeV electron LINAC installed at Hokkaido University. The dynamical effect in the high Q region was succesfully corrected by the method proposed by one of the authors based on the Wick's short time approximation. The structure factor $S(Q)$ of liquid methanol was obtained over a wide range of Q ($1 \sim 30 Å^{-1}$). The intramolecular structure, which can be derived from $S(Q)$ in the high Q region, was examined by comparing with model calculations.

1. Introduction

The neutron diffraction method by means of an electron linear accelerator (LINAC) is one of the most powerful methods for the investigation of a structure of liquids containing hydrogen, because, by the method, light nuclei can be seen and the high Q (momentum transfer) region can be easily measured.

The dynamical correction is important in the high Q region where the inelastic scattering effect becomes more significant, especially for light nuclei. The conventional method for the dynamical correction proposed by Placzek[1], is not applicable to systems containing light nuclei because the method is based on the expansion in powers of the inverse mass of target nucleus.

Although the structure of liquid methanol has been studied by the X-ray diffraction method[2], no neutron diffraction study has been reported to the best of the authors knowledge. We have performed the neutron diffraction experiment of liquid methanol by the time-of-flight (TOF) method with the 45 MeV electron LINAC installed at Hokkaido University[3]. The dynamical effect in the high Q region was treated by the correction method[4] proposed by one of the present authors, Matsumoto, which, based on the Wick's short time approximation[5], is also applicable to light nuclei. The structure factor $S(Q)$ was obtained in a wide range of Q ($1 \sim 30$ $Å^{-1}$). The intramolecular structure of liquid methanol was examined in comparison with model calculations.

2. The Structure Factor of Molecular Liquids

The structure of liquid is described by the structure factor $S(Q)$,

* Department of Atomic Engineering.

$$S(Q)=\sum_{ll'}\bar{b}_l\bar{b}_{l'}\langle e^{i\boldsymbol{Q}\cdot(\boldsymbol{r}_l-\boldsymbol{r}_{l'})}\rangle\,, \tag{2-1}$$

where $\hbar\boldsymbol{Q}$: momentum transfer
b_l: scattering length of nucleus l
$\boldsymbol{r}_l$: position vector of nucleus l
$\langle\ \rangle$: time average
and the summation by l and l' is taken over all the nuclei in the sample.

Let the vector $\boldsymbol{r}_l$ be represented by the sum of the position vector of the molecule i containing the nucleus $l\,(\boldsymbol{R}_i)$ and the vector from the center of the molecule i to the nucleus $l\,(\boldsymbol{r}_\alpha)$, namely,

$$\boldsymbol{r}_l\longrightarrow\boldsymbol{R}_i+\boldsymbol{r}_\alpha\,.$$

Then, $S(Q)$ can be rewritten in the form,

$$\begin{aligned}S(Q)&=\sum_{ij}^{N_m}\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta\langle e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_{ij}+\boldsymbol{r}_{\alpha\beta})}\rangle\\&=N_m\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta\langle e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_{\alpha\beta}}\rangle+\sum_{i\neq j}^{N_m}\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta\langle e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_{ij}+\boldsymbol{r}_{\alpha\beta})}\rangle\\&=N_m(\sum_\alpha\bar{b}_\alpha)^2\Big\{F_1(Q)+D_m(Q)\Big\}\,,\end{aligned} \tag{2-2}$$

where
$$\begin{aligned}F_1(Q)&\equiv(\sum_\alpha\bar{b}_\alpha)^{-2}\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta\langle e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_{\alpha\beta}}\rangle\\&=(\sum_\alpha\bar{b}_\alpha)^{-2}\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta\frac{\sin Qr_{\alpha\beta}}{Qr_{\alpha\beta}}\,e^{-W_{\alpha\beta}(Q)}\end{aligned}$$

$$D_m(Q)=\Big\{N_m(\sum_\alpha\bar{b}_\alpha)^2\Big\}^{-1}\sum_{i\neq j}^{N_m}\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta\langle e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_{ij}+\boldsymbol{r}_{\alpha\beta})}\rangle$$

$$\boldsymbol{R}_{ij}=\boldsymbol{R}_i-\boldsymbol{R}_j\,,\qquad \boldsymbol{r}_{\alpha\beta}=\boldsymbol{r}_\alpha-\boldsymbol{r}_\beta$$

$e^{-W_{\alpha\beta}(Q)}$: Debye-Waller factor
N_m: number of molecules in the sample
and the summation by α and β is taken in the single molecule.

The molecular form factor $F_1(Q)$ represents the intramolecular correlational part and $D_m(Q)$ the intermolecular one. In the high Q region, i.e., in the short wavelength, where $\lim_{Q\to\infty}D_m(Q)\to 0$, so that $S(Q)\propto F_1(Q)$. In other words, the intramolecular structure can be determined from the high Q region.

3. The Data Processing of Neutron Diffraction of Molecular Liquids

3.1 The Count Ratio

The neutron count $C(2\theta, t)$ measured at the scattering angle 2θ and time t is given by the following expression in the case of neutron diffraction method by LINAC,

$$C(2\theta,t)=a\int_{-\infty}^{\infty}dEdE_0\varepsilon(E)\,\phi(E_0)\,\frac{k}{k_0}\,S(Q,\omega)\,\delta\Big(t-\frac{L_0}{v_0}-\frac{L}{v}\Big), \tag{3-1}$$

where $\varepsilon(E)$: detector efficiency
$\phi(E_0)$: incident neutron spectrum
$S(Q,\omega)$: scattering function
L: length of neutron flight path
E: neutron energy
v: neutron velocity
k: neutron wave number
a: constant
$\omega=(E_0-E)/\hbar$
and subscript $\circ$ represents the value for incident neutron.

The scattering function $S(Q,\omega)$ is written as follows,

$$S(Q,\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\sum_{\alpha\beta}\overline{b_\alpha b_\beta}\langle e^{iQ\cdot r_\alpha(t)}\, e^{-iQ\cdot r_\beta(0)}\rangle\,. \tag{3-2}$$

Furthermore, $S(Q,\omega)$ can be separated into two parts,

$$\begin{aligned}S(Q,\omega)&=S^{\mathrm{self}}(Q,\omega)+S^{\mathrm{int}}(Q,\omega)\\&=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\sum_{\alpha}\overline{b_\alpha^2}\langle e^{iQ\cdot r_\alpha(t)}\, e^{-iQ\cdot r_\alpha(0)}\rangle\\&+\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\sum_{\alpha\neq\beta}\bar{b}_\alpha\bar{b}_\beta\langle e^{iQ\cdot r_\alpha(t)}\, e^{-iQ\cdot {}_\beta(0)}\rangle\,,\end{aligned} \tag{3-3}$$

and alternatively,

$$\begin{aligned}S(Q,\omega)&=S^{\mathrm{inc}}(Q,\omega)+S^{\mathrm{coh}}(Q,\omega)\\&=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\sum_{\alpha}(\overline{b_\alpha^2}-\bar{b}_\alpha^2)\langle e^{iQ\cdot r_\alpha(t)}\, e^{-iQ\cdot r_\alpha(0)}\rangle\\&+\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta\langle e^{iQ\cdot r_\alpha(t)}\, e^{-iQ\cdot r_\beta(0)}\rangle\,.\end{aligned} \tag{3-4}$$

The structure factor $S(Q)$ is derived from the integration of the coherent scattering function $S^{\mathrm{coh}}(Q,\omega)$ over ω,

$$S(Q)=\int_{-\infty}^{\infty}d\omega\, S^{\mathrm{coh}}(Q,\omega)\,. \tag{3-5}$$

Integrating Eq. (3-1) over E_0, we obtain

$$C(2\theta,t)=\frac{a(1-\gamma)}{L_0}\int_{-\infty}^{\infty}d\omega\,\frac{k^4k_0^2}{\gamma k_0^3+(1-\gamma)k^4}\,\varepsilon(E)\,\phi(E_0)\,S(Q,\omega)\,, \tag{3-6}$$

where $\gamma=L/(L_0+L)$.

Since vanadium can be considered as an incoherent elastic scatterer, its scattering function $S_v(Q,\omega)$ is given by,

$$S_v(Q,\omega)=N_v\overline{b_v^2}\,\delta(\omega)\,. \tag{3-7}$$

From Eqs. (3-6) and (3-7), the count for vanadium $C_v(2\theta,t)$ results in,

$$C_v(2\theta,t)=\frac{a(1-\gamma)}{L_0}\,N_v\overline{b_v^2}k_e^3\,\varepsilon(E_e)\,\phi(E_e)\,, \tag{3-8}$$

where subsctipt e represents elastic scattering.

Dividing Eq (3-6) by Eq. (3-8), the count ratio $R(2\theta, Q_e)$ of the sample to vanadium is given by,

$$R(2\theta, Q_e) = \frac{C(2\theta, t)\, dt/dQ_e}{C_v\,(2\theta, t)\, dt/dQ_e}$$

$$= (N_v \overline{b_v^2})^{-1} \int_{-\infty}^{\infty} d\omega\, A(k)\, S(Q, \omega)\,, \tag{3-9}$$

where
$$A(k) = \frac{\left(\frac{k}{k_e}\right)^4 \left(\frac{k_0}{k_e}\right)^2 \varepsilon(E)\, \phi(E_0)}{\gamma\left(\frac{k_0}{k_e}\right)^3 + (1-\gamma)\left(\frac{k}{k_e}\right)^3 \varepsilon(E_e)\, \phi(E_e)}\,. \tag{3-10}$$

If the sample is the elastic scatterer, $A(k)=1$ and $S^{\mathrm{coh}}(Q, \omega) = S(Q)\delta(\omega)$, then the integration of the coherent part of Eq. (3-9) becomes

$$\int_{-\infty}^{\infty} d\omega\, S(Q)\, \delta(\omega) = S(Q_e)\,. \tag{3-11}$$

Therefore the structure factor $S(Q_e)$ can be directly obtained from the coherent part of the count ratio $R(2\theta, Q_e)$.

In liquids, however, the inelastic scattering always occurs and a correction is necessary for the deviation from $A(k)=1$. This is called the dynamical correction.

3.2 The Dynamical Correction[4)]

Wick proposed an approximation method of the calculation of the neutron scattering from systems containing light nuclei, based on an assumption that the collision time is short for the high energy transfer of the incident neutron. One of the authors applied Wick's method to the dynamical correction for the neutron diffraction experiment on LINAC.

By the short time approximation, $S^{\mathrm{self}}(Q, \omega)$ is written as the following expression[5)],

$$S^{\mathrm{self}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} N_m \sum_{n\alpha} \overline{b_\alpha^2} \left(\frac{it}{n!}\right)^n S_n(Q^2)\, e^{iQ^2 t/2M_\alpha}\,, \tag{3-12}$$

where
$$s_0 = 1\,, \qquad s_1 = 0\,, \qquad s_2 = \frac{2}{3}\langle K\rangle \frac{Q^2}{M_\alpha}$$

$$s_3 = \langle B\rangle \frac{Q^2}{2M_\alpha}\,, \qquad s_4 = \frac{4}{5}\langle K^2\rangle \frac{Q^4}{M_\alpha^2} + \langle C\rangle \frac{Q^2}{M_\alpha}\,.$$

The symbols are same as in Ref. 3.

If the flight path ratio γ is small (3.2% for our apparatus), $A(k)$ in Eq. (3-10) can be expanded in powers of γ. And if the efficiency of the detector obeys $1/v$ law and the incident spectrum $1/E$ law, the self term of Eq. (3-9) becomes

$$\int_{-\infty}^{\infty} d\omega\, A(k)\, S^{\mathrm{self}}(Q, \omega) = N_m (\sum_\alpha \bar{b}_\alpha)^2 \sum_{n=0}^{3} P_n\, k_e^{-2n}\,, \tag{3-13}$$

where
$$P_0 = \sum_\alpha \overline{b_\alpha^2} \frac{\phi_{00}}{(\sum_\alpha \bar{b}_\alpha)^2}$$

$$P_1 = \frac{4}{3}\langle K\rangle \sum_\alpha \frac{\overline{b_\alpha^2}}{M_\alpha} \frac{\phi_{31}}{(\sum_\alpha \bar{b}_\alpha)^2}$$

$$P_2=-\frac{2}{3}\langle B\rangle\sum_\alpha\frac{\overline{b_\alpha^2}}{M_\alpha}\frac{\psi_{13}}{(\sum_\alpha\bar{b}_\alpha)^2}+\frac{8}{15}\langle K^2\rangle\sum_\alpha\frac{\overline{b_\alpha^2}}{M_\alpha^2}\frac{\psi_{42}}{(\sum_\alpha\bar{b}_\alpha)^2}$$

$$P_3=\frac{2}{3}\langle C\rangle\sum_\alpha\frac{\overline{b_\alpha^2}}{M_\alpha}\frac{\psi_{41}}{(\sum_\alpha\bar{b}_\alpha)^2}.$$

$S^{\text{int}}(Q,\omega)$ is also written in the following form by the short time approximation[5],

$$S^{\text{int}}(Q,\omega)=\frac{1}{2\pi}\sum_{n,l\neq l'}\bar{b}_l\bar{b}_{l'}\frac{g_n^{ll'}}{n!}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}(it)^n, \tag{3-14}$$

where $g_0^{ll'}=\langle e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_{ll'}}\rangle$, $g=0$

$$g_2=\frac{Q^4 g_0^{ll'}}{4M_l M_{l'}}+\frac{1}{M_l M_{l'}}\langle e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_{ll'}}(\boldsymbol{Q}\cdot\boldsymbol{P}_l)(\boldsymbol{Q}\cdot\boldsymbol{P}_{l'})\rangle.$$

From Eq. (3-14), the interference term of Eq. (3-9) becomes

$$\int_{-\infty}^{\infty}d\omega\,A(k)\,S^{\text{int}}(Q,\omega)=N_m(\sum_\alpha\bar{b}_\alpha)^2\left\{S(Q_e)-\frac{\sum_\alpha\bar{b}_\alpha^2}{(\sum_\alpha\bar{b}_\alpha)^2}+\frac{1}{8}\frac{d^2}{d\omega^2}\Big[Q^4A(k)\,S'(Q)\Big]_{\omega=0}\right\}, \tag{3-15}$$

where $$S'(Q)=\frac{1}{N_m(\sum_\alpha\bar{b}_\alpha)^2}\sum_{l\neq l'}\frac{\bar{b}_l\bar{b}_{l'}}{M_l M_{l'}}\langle e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_{ll'}}\rangle.$$

From Eqs. (3-13) and (3-15),

$$R(2\theta,Q_e)=\frac{N_m(\sum_\alpha\bar{b}_\alpha)^2}{N_v\overline{b_v^2}}\left\{S(Q_e)-\frac{\sum_\alpha\bar{b}_\alpha^2}{(\sum_\alpha\bar{b}_\alpha)^2}+\sum_{n=0}^{3}P_n\,k_e^{-2n}+\frac{1}{8}\frac{d^2}{d\omega^2}\Big[Q^4A(k)\,S'(Q)\Big]_{\omega=0}\right\}. \tag{3-16}$$

Obtaining the count ratio $R(2\theta,Q_e)$ from the experiment, the structure factor $S(Q_e)$ is derived from Eq. (3-16). The 4th term of r. h. s. of Eq. (3-16) can be neglected as it may be considered to be small. The coefficients P_n in the 3rd term are experimentally determined from the inclination of the count ratio $R(2\theta,Q_e)$ in the high Q region, because the dependence of the 3rd term on Q is much smoother than that of the 1st one.

4. Neutron Diffraction Experiment

As has been stated before, the experiment was performed by the neutron diffraction apparatus of the TOF method using the 45 MeV electron LINAC of Hokkaido University as a pulsed neutron source[3].

The electron pulse from the LINAC is injected into a Pb target to produce bremsstrahlung. The pulsed fast neutrons generated by the $(\gamma-n)$ reaction are moderated and thermalized through light water to become the pulsed thermal neutrons.

After flying through the pipe in the concrete shield, these neutrons are scattered by a sample and detected by He-3 counters. The energy of neutron is analyzed by the measurement of its flight time. In the present experiment, the LINAC is operated under the conditions of the pulse width 3 μsec and the pulse rate 100 pps. The length of flight path are 693 cm from the moderator to the sample and 23 cm from the sample to the counters, respectively.

The sample used in this experiment is deuterated methanol provided by CEA

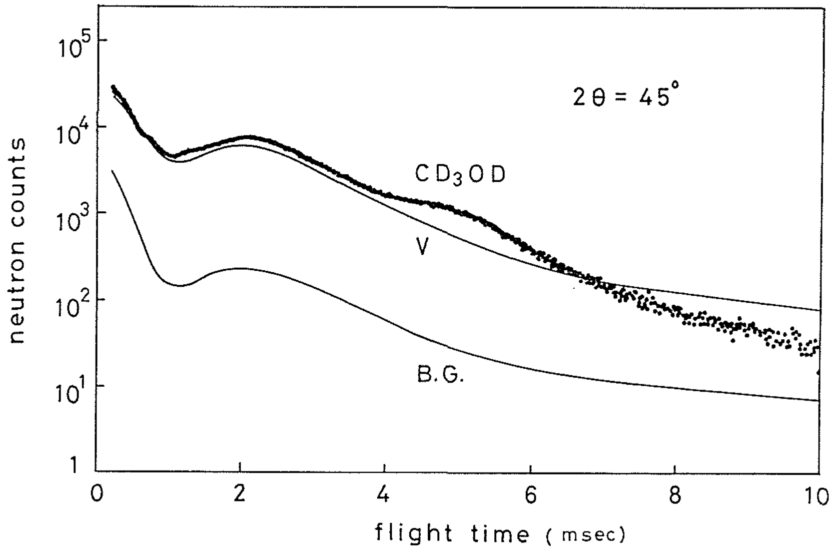

Fig. 1. TOF spectrum of liquid methanol at $2\theta=45°$. Spectra of vanadium and background are normalized to that of methanol after smoothing.

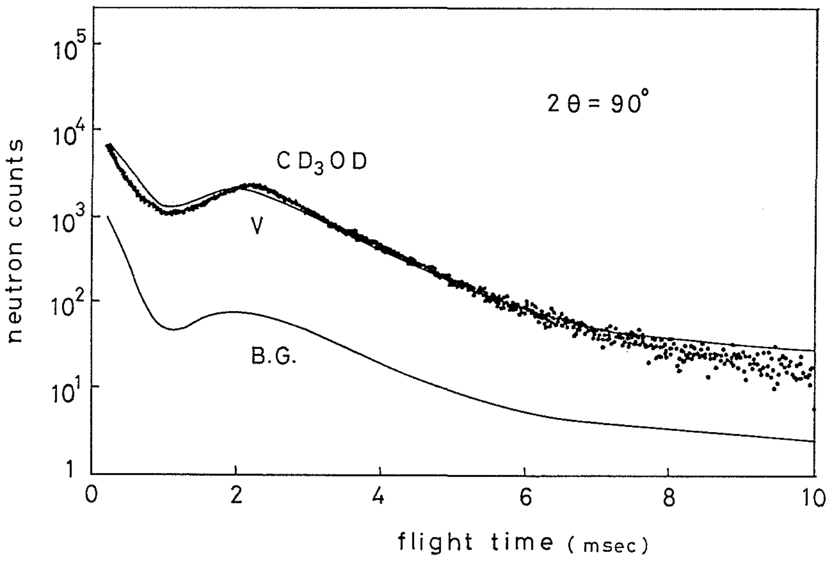

Fig. 2. TOF spectrum of liquid methanol at $2\theta=90°$.

(deuterium enrichment=99.4%). The sample container is a cylinder (10 mmϕ) of vanadium with 0.05 mm thickness. The scattering angle is set up at three points: $2\theta=45°$, $90°$ and $150°$ for obtaining the data with high quality in the wide range of Q.

The TOF spectra of methanol at room temperature are shown in Fig. 1~3. In comparison with vanadium, the peaks which reflect the structure of methanol are clearly seen.

Figure 4 shows the neutron count ratio $R(2\theta, Q)$ at $2\theta=150°$, converting the time axis to the Q one. If the sample has little dynamical effect, $R(2\theta, Q)$ might approach a constant value in the high Q region. However, it is clearly seen that

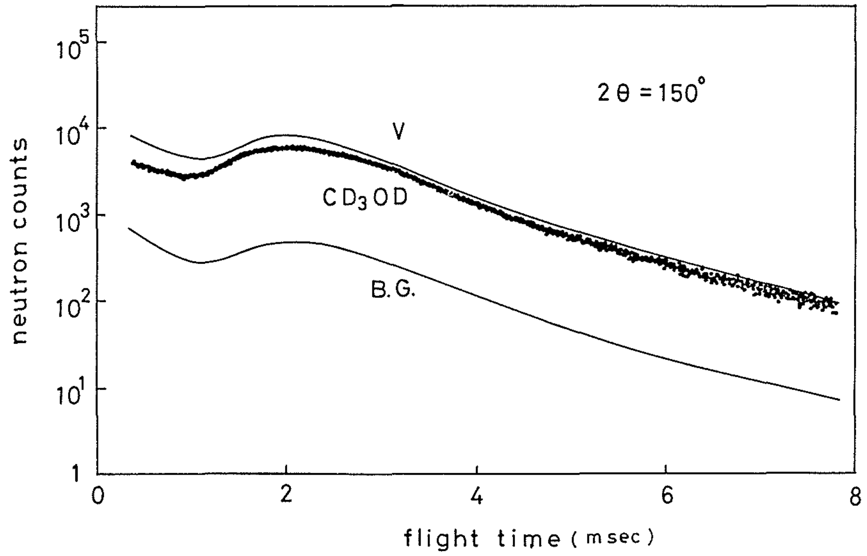

Fig. 3. TOF spectrum of liquid methanol at $2\theta=150°$.

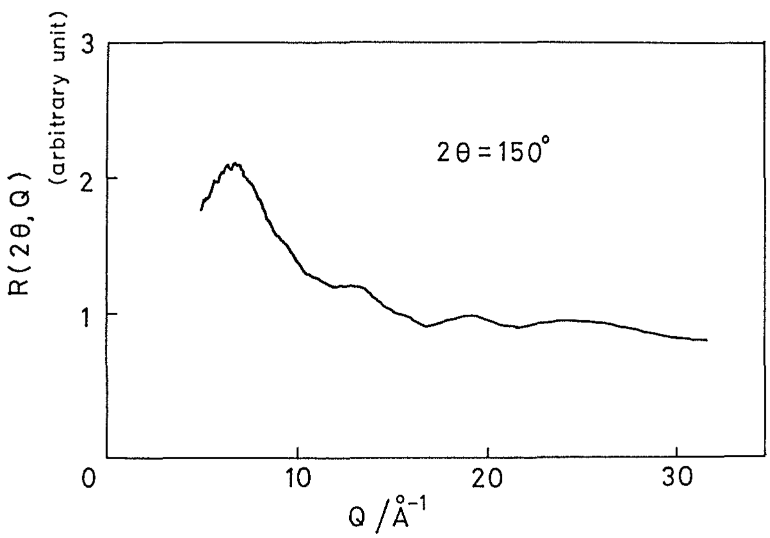

Fig. 4. Count ratio of liquid methanol to vanadium at $2\theta=150°$.

the value of $R(2\theta, Q)$ decreases as Q increases.

The structure factor $S(Q)$ obtained after the dynamical correction of Eq. (3-16) is shown in Fig. 5. This $S(Q)$ is made of data at the different scattering angles: $Q>19$ Å^{-1}; $2\theta=150°$, $8<Q<19$ Å^{-1}; $2\theta=90°$ and $Q<8$ Å^{-1}; $2\theta=45°$. $S(Q)$ is shown to approach a constant value as Q becomes large, which proves that the dynamical correction is appropriate. $S(Q)$ of Eq. (2-2) is divided by $N_m(\sum_\alpha \bar{b}_\alpha)^2$ in order to

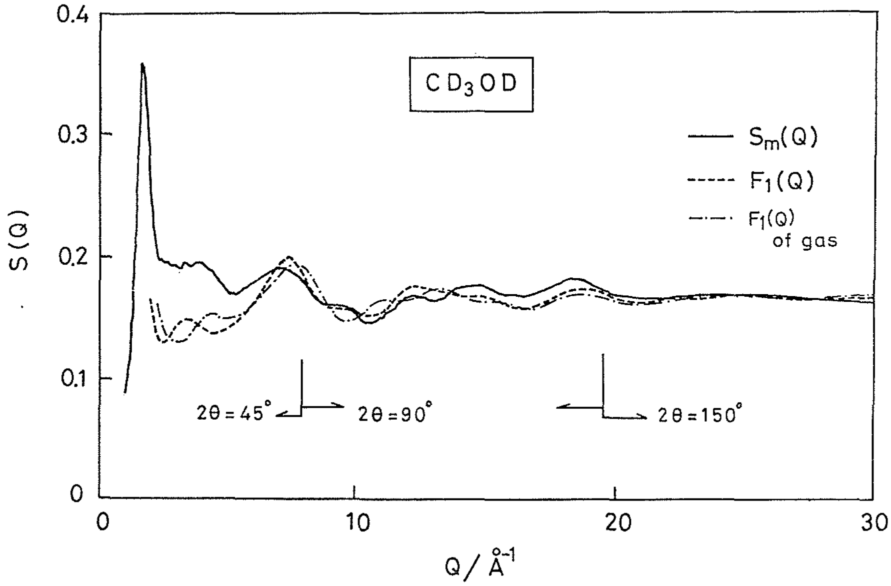

Fig. 5. Structure factor $S(Q)$ and molecular form factor $F_1(Q)$ for liquid methanol: —— $S(Q)$, ------ $F_1(Q)$ with modified parameters and -·-·- $F_1(Q)$ with the parameters of gas phase.

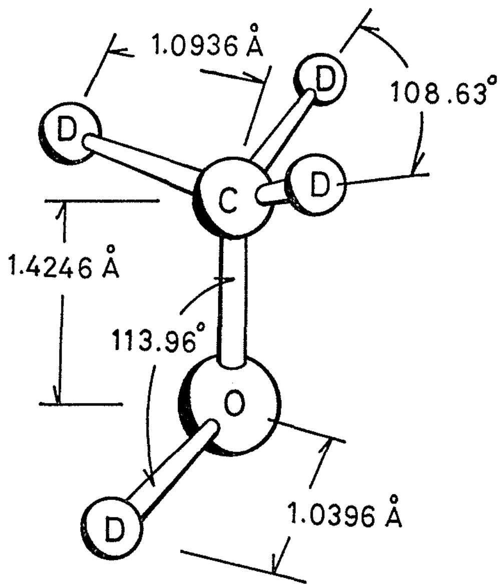

Fig. 6. Molecular structure of liquid methanol.

normalize to the value related to one molecule, namely,

$$S(Q) = F_1(Q) + D_m(Q)\,. \tag{4-1}$$

The model calculation of $F_1(Q)$ is also shown in Fig. 5. The methyl group is assumed to be rotating freely around its axis. The function $W_{\alpha\beta}(Q)$ in the Debye-Waller factor is evaluated by the equation,

$$W_{\alpha\beta}(Q) = ar_{\alpha\beta}\,Q^2\,,$$

where a is a constant (0.002 Å).

Under these conditions, $F_1(Q)$ of methanol can be written as follows,

$$\begin{aligned} F_1(Q) = \Big[& \bar{b}_C^2 + \bar{b}_O^2 + 4\bar{b}_D^2 \\ & + 2\Big\{\bar{b}_C\,\bar{b}_O\,j_0(Qr_{CO})\,e^{-ar_{CO}Q^2} + \bar{b}_C\,\bar{b}_D\,j_0(Qr_{CD})\,e^{-ar_{CD}Q^2} \\ & \quad + \bar{b}_O\,\bar{b}_D\,j_0(Qr_{OD})\,e^{-ar_{OD}Q^2}\Big\} \\ & + 6\Big\{\bar{b}_C\,\bar{b}_D\,j_0(Qr_{CD_M})\,e^{-ar_{CD_M}Q^2} + \bar{b}_O\,\bar{b}_D\,j_0(Qr_{OD_M})\,e^{-ar_{OD_M}Q^2} \\ & \quad + \bar{b}_D^2\,j_0(Qr_{DD_M})\,e^{-ar_{DD_M}Q^2} + \bar{b}_D^2\,j_0(Qr_{D_MD_M})\,e^{-ar_{D_MD_M}Q^2}\Big]\Big/ \\ & (\bar{b}_C + \bar{b}_O + 4\bar{b}_D)\,, \end{aligned} \tag{4-2}$$

where $j_0(x) = \sin(x)/x$
and D_M represents D of methyl group.

The parameters used in this calculation are the gas phase data[6] modified to fit the experimental value. They are tabulated in Table 1. The values r_{OD} and ∠COD are respectively 10% and 5% larger than that of the gas phase. Figure 6 illustrates the molecular structure of liquid methanol with these parameters.

$F_1(Q)$ with the modified parameters shows a good agreement with the experimental $S(Q)$ in the high Q region. In the low Q (<7 Å^{-1}), $S(Q)$ deviates from $F_1(Q)$ because the contribution of the intermolecular correlation $D_m(Q)$ becomes significant.

Table 1. Parameters for molecular structure of methanol

gas (CH_3OH) (Ref. 6)	liquid (CD_3OD) (this paper)	liquid (CH_3OH) (Ref. 2)
$C-H_M$: 1.0936 Å	$C-D_M$: 1.0936 Å	
$C-O$: 1.4246 Å	$C-O$: 1.4246 Å	$C-O$: 1.5 Å
$O-H$: 0.9451 Å	$O-D$: 1.0396 Å	
$\angle H_MOH_M$: 108.63°	$\angle D_MOD_M$: 108.63°	
$\angle COH$: 108.53°	$\angle COD$: 113.96°	

Subcript M represents methyl group.

5. Conclusion

The neutron diffraction experiment for liquid methanol was performed by the LINAC-TOF method, and the structure factor $S(Q)$ was obtained in the wide range of Q ($1\sim30$ Å^{-1}) after making the dynamical correction proposed by one of the present authors, Matsumoto.

The intramolecular structure of liquid methanol was derived from the structure factor in the high Q region. Although the structure of liquid methanol has been studied by the X-ray diffraction method, where the position of hydrogen can not be determined explicitly. The present experiment with neutron diffraction method ennabled us to determine it, for the first time.

These results proved that the neutron diffraction method with a LINAC is a powerful tool for the investigation of the intramolecular structure of liquids containing hydrogen.

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