Liquid Structure of SO$_2$ from X-Ray and Neutron Diffraction

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X-Ray and neutron scattering measurements on liquid SO$_2$ were performed at 258 and 293 K, respectively. The intramolecular distances within SO$_2$ molecules in the liquid state were determined as 1.42(1) Å (S—O) and 2.47(3) Å (O—O), which do not differ significantly from those found in the gaseous and in the crystalline states. The radial distribution functions obtained by both these methods showed the presence of preferred orientational correlation between SO$_2$ molecules in the liquid. Experimental intensities were satisfactorily explained by a body-center-cubic cluster model in which there were fifteen SO$_2$ molecules with the first neighbour SO$_2$—SO$_2$ distance=4.25 Å.

The structure of liquid sulfur dioxide and of equilibrium species resulting from the dissolution of sulfur dioxide into water, has been of considerable interest in connection with research on SO$_2$-induced atmospheric corrosion and catalytic oxidation of SO$_2$ in polluted air.[1,2] Previously we have reported the structure of sulfate, sulfite and disulfite ions in aqueous solution determined by an X-ray diffraction method.[3] Since sulfur dioxide is an important solvent in chemical syntheses, it also seemed worthwhile to investigate the liquid structure of sulfur dioxide in order to clarify its physico-chemical properties such as conductivity and chemical reactivity. The structure of sulfur dioxide previously has been determined only in the gaseous and in the solid states. Electron diffraction[4] and microwave spectroscopic studies[5] of gaseous SO$_2$ have shown that the

sulfur dioxide molecule has a C_{2v} symmetry. In the solid state, sulfur dioxide molecules are arranged in a nearly face-center-cubic structure.[6,7] Raman and infrared spectra of liquid sulfur dioxide have been measured[8,9] but the details of the liquid structure have not been deduced.

In the present study we have used X-ray and neutron diffraction techniques to determine the structure of liquid sulfur dioxide. In the present system X-ray diffraction emphasizes the contribution from sulfur atoms, while that from oxygen atoms is predominant in neutron diffraction. Thus, combined X-ray and neutron scattering measurements may yield a definite conclusion on the structure of liquid SO$_2$.

EXPERIMENTAL AND DATA ANALYSIS

The sample of liquid sulfur dioxide was prepared by cooling commercially available gaseous SO$_2$, which had been bubbled in concentrated sulfuric acid, by a cryostat or a freezing mixture of alcohol and solid CO$_2$.

Cryostat. The arrangement of the cryostat is shown in Fig. 1. The inside sample chamber was cooled by circulating cold dry N$_2$ gas passed through liquid N$_2$. The chamber has a 15 mm wide window covered with a Melinex film (125 μ). The sample chamber was placed inside an air-tight cylindrical radiation shield having a 15 mm wide opening with a Melinex film (125 μ) window and *in vacuo* during the measurements. The temperature was carefully controlled within ±1 °C by regulating the flow rate of N$_2$ gas. The copper-constantan thermocouple was used to check the temperature of the sample.

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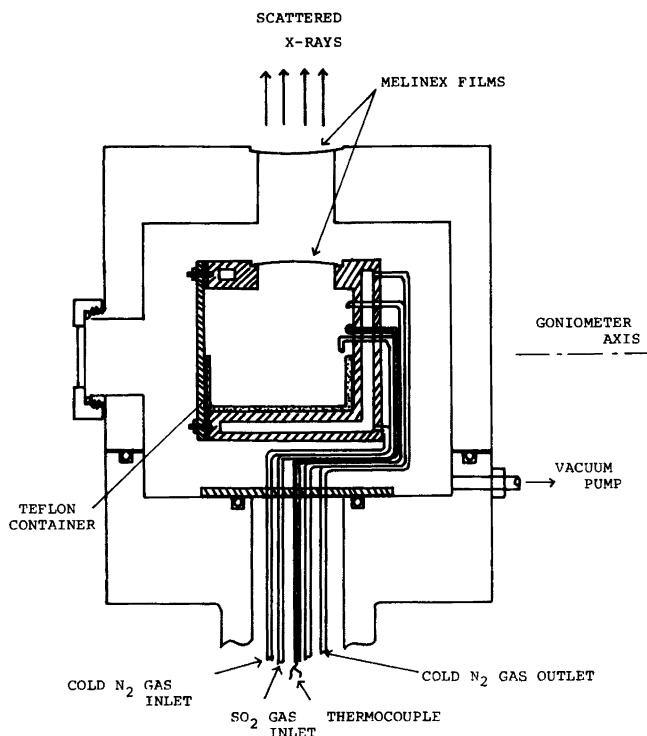
Fig. 1. Cross-sectional drawing of the cryostat.

X-Ray measurements. X-Ray scattering measurements were carried out at 258 K (5 degrees below the boiling point) using reflection geometry. The Mo$K\alpha$ radiation ($\lambda=0.7107$ Å) was used with an LiF crystal monochromator in the diffracted beam. Experimental intensities were measured at discrete points in the scattering range $2°<2\theta<120°$, corresponding to the range 0.2 Å$^{-1}<k<16.0$ Å^{-1} ($k=4\pi\sin\theta/\lambda$). The whole range was scanned twice, so that total 20000 counts were collected at each angle with several combinations of beam divergences and increment angles. The details of the diffractometer and the measurements have been described previously.[3]

Experimental intensities were corrected for background, absorption in the sample, polarization, multiple scattering and Compton (incoherent) scattering in the usual manner[3] and were then scaled to absolute electron units by comparing the observed intensities with the independent scattering in a high angle region ($k>13.5$ Å^{-1}). The scattering factors for neutral atoms were taken from the International Tables.[10] The values for incoherent scattering factors were taken from those given by Cromer[11] and corrected for the Breit-Dirac effect. The values for anomalous

scattering were taken from the International Tables.[10] The structure function $i(k)$ was obtained by eqn. (1).

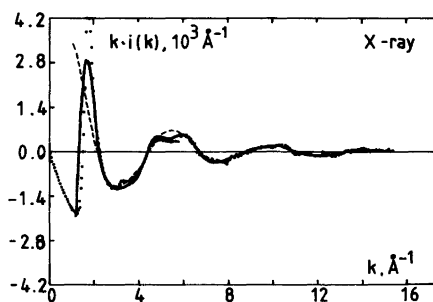$$i(k)=I(\mathrm{k})-\sum x_i f_i^2(k) \tag{1}$$

Fig. 2. The structure function $k \cdot i(k)$ obtained by X-ray diffraction at 258 K. Dots show the observed values and the solid line the calculated ones for the bcc cluster model. The dashed line represents the contribution of the intramolecular interaction.

Here $I(k)$ is the scaled observed intensites, f_i is the scattering factor of the ith atom and x_i is the number of the ith atom in the stoichiometric unit of volume V containing one SO$_2$ molecule. The structure function $i(k)$, multiplied by k, is shown in Fig. 2. The electronic radial distribution function was calculated by eqn. (2).

$$D(r)=4\pi r^2\rho_0+\frac{2r}{\pi}\int_{kmin}^{kmax} k\cdot i(k)M(k)\sin(rk)dk \quad (2)$$

Here, $M(k)$ is the modification function$[f_S^2(0)/f_S^2(k)]\times \exp(-0.01k^2)$, in which the exponential term was included to reduce the termination effect in the Fourier transformation, and the average scattering density $\rho_0=[\sum x_i f_i(0)]^2/V$. k_{min} and k_{max} are the lower and the upper limits of k available in the measurements.

A theoretical structure function based on a model employed was calculated by eqn. (3).

$$i(k)_{mod}=\sum x_i\sum\sum n_{ij}f_if_j\sin(kr_{ij})/(kr_{ij})\exp(-l_{ij}^2k^2/2) \quad (3)$$

Eqn. (3) takes into account only the contribution from short-range discrete structures with the distance r_{ij}, the root-mean-square (rms) variation l_{ij} to r_{ij}, and the number of interactions n_{ij}. These calculations were performed by program KURVLR.[12]

Neutron measurements. The neutron diffraction pattern was obtained in transmission geometry. Gaseous SO$_2$ was transferred into a quartz tube (the inner diameter was 5.3 mm, the height 60 mm and the thickness 0.5 mm), where it was condensed by a mixture of alcohol and solid CO$_2$. When the sample cell was filled at a satisfactory level, it was sealed off *in vacuo.* A segment of 4 cm of the sample cell was immersed in the neutron beam. The sample was mounted on one of the crystal diffractometers at the Studsvik reactor. The measurements were performed at 293 K. The Cu monochromator was used to select the wave length of the incident neutrons of 0.968 Å. The range of the scattering angles covered was $2°<2\theta<96.8°$, corresponding to the range $0.2 \text{ Å}^{-1}<k<9.7 \text{ Å}^{-1}$ with a resolution of 0.05 Å^{-1} in almost all ranges. The increment of the angle was 0.3 degree in the whole scan range.

The measured neutron intensities were corrected for air scattering, absorption in the sample, scattering and absorption by the quartz cell, multiple scattering[13] and incoherent scattering. The correction for the inelastic effect (the Placzek correction) was performed as described by Yarnell *et al.,*[14] as no satisfactory model to describe the molecular motion in liquid SO$_2$ is
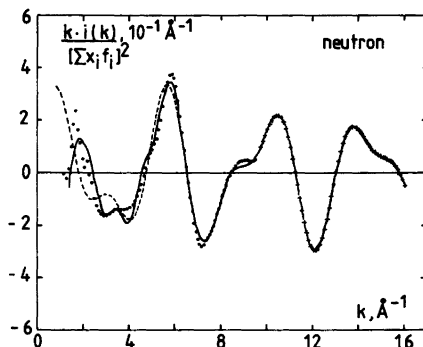
Fig. 3. The structure function $k\cdot i(k)/[\sum x_i f_i]^2$ obtained by neutron diffraction at 293 K. Dots show the observed values and the solid line the calculated ones for the bcc cluster model. The sign of the cross and the dashed line represent the contribution of the intramolecular interaction.

available.[15] The normalization of the data to the absolute cross section units was performed using the scattering from a solid vanadium cylinder with the same dimension as the sample container. The experimental neutron structure function $i(k)$, multiplied by $k/[\sum x_i f_i]^2$ (f_i is the scattering length of the ith nucleus), is shown in Fig. 3. The scattering lengths of nuclei S and O were taken from the literature.[16]

The radial distribution function was obtained using eqn. (2) as in the X-ray case. Since the k_{max} value was about 10 Å^{-1} in the present neutron measurement, the Fourier transform of the $k\cdot i(k)[\sum x_i f_i]^{-2}$ values might suffer from the truncation error. Therefore, the calculated structure function using eqn. (3) with the intramolecular parameters obtained by the least-squares fits described later, was added up to $k=16$ Å^{-1} and then the total structure function was Fourier transformed. The modification function $(M(k)$ used was $[\sum x_i f_i]^{-2}\exp(-0.01k^2)$ and ρ_0 was taken as the molecular number density.

The synthetic structure function for a model assumed was calculated by eqn. (3) as described before.

RESULTS AND DISCUSSION

Radial distribution functions (RDFs). The radial distribution functions of the form $D(r)-4\pi r^2\rho_0$ obtained by the X-ray and neutron measurements are shown in Figs. 4 and 5, respectively. The first peak around 1.42 Å in both figures is certainly ascribed to the S$-$O
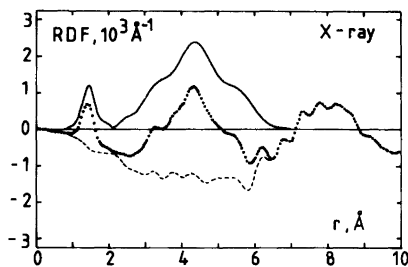
Fig. 4. The radial distribution function obtained by X-ray diffraction at 258 K. Dots show the observed values and the solid line the calculated ones for the bcc cluster model. Their difference is shown by the dashed line.
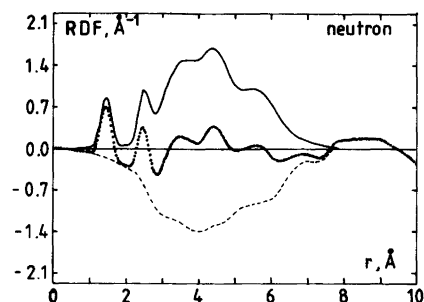

Fig. 5. The radial distribution function obtained by neutron diffraction at 293 K. Dots show the observed values and the solid line the calculated ones for the bcc cluster model. Their difference is shown by the dashed line.

bonds within an SO_2 molecule. The second peak at 2.4 Å in Fig. 5 corresponds to the O−O interaction within the SO_2 molecule. This O−O peak is not seen in Fig. 4 as expected. Fig. 4 shows the large distinct peak centered at 4.25 Å with a small hump at 3.2 Å and a shoulder at around 5.5 Å. Since the contribution of sulfur atoms is predominant in the present X-ray case, the 4.25 Å peak is expected to be due to S−S interactions between nearest-neighbour SO_2 molecules in the liquid. In the crystal structure of SO_2,[6,7] the S−S distance between adjacent SO_2 molecules has been reported to be 4.25−4.27 Å, well consistent with the value found in the present study. Thus, we assigned this peak to the S−S atom pairs with the intermolecular ·SO_2−SO_2 interactions. In the RDF obtained in the neutron measurement (Fig. 5), peaks are seen at around 3.5, 4.4 and 5.6 Å. These peaks also arise from the intermolecular SO_2−SO_2 interactions. The appearance of the three peaks as well as the small hump (3.2 Å) and the

shoulder (5.5 Å) seen in the X-ray RDF might indicate the presence of some specific orientation between the neighbouring SO_2 molecules, details of which are described later.

Molecular structure. In general, intramolecular interaction is difficult to separate from intermolecular interaction. However, the latter vanishes rapidly with increasing k value, so that the parameters of a molecular structure may be obtained from a least-squares fitting procedure applied to the structure functions $i(k)$. We minimized a function $U=\sum k^2[i(k)_{obs}-i(k)_{mod}]^2$ with the distance r_{ij}, the rms variation l_{ij} as parameters optimized. The program NLPLSQ[17] was used in the calculations. The k-ranges taken in the least-squares fits were $4.0<k<16.0$ Å^{-1} and $4.0<k<9.7$ Å^{-1} for the X-ray and neutron structure functions, respectively. The final results are given in Table 1, together with the values obtained in the gas and in the solid phases. The S−O distances obtained by the both methods

Table 1. Structural parameters for the intramolecular interactions. The values in parentheses are their estimated standard deviations. The units on r and l are in Å.

		Crystal[7]	Liquid[a] X-Ray	Neutron	Gas Electron[4]	Microwave[5]
S−O	r	1.43(2)	1.42(1)	1.42(2)	1.4343(3)	1.432
	l		0.045(2)	0.04(2)	0.036(1)	
O−O	r	2.46(1)		2.47(3)	2.472(3)	
	l			0.06(3)	0.056(3)	
O−S−O (°)		120(2)		121(3)	119.5(3)	

[a] This work.

Table 2. Interatomic distances (Å) in two types of configurations (a and b shown in Fig. 6) found in the crystal structure of SO_2.[7] The positions of the peaks in the RDFs are also listed.

Configurations (a)		(b)		RDF X-Ray	Neutron
S−O	3.10	S−O	3.25	3.2	
2×O−O	3.26	O−O	3.70		3.5
S−S	4.25	S−S	4.27	4.3	
S−O	4.47	2×O−O	4.27		4.4
S−O	4.50	S−O	4.41		
S−O	5.52	S−O	4.60		
O−O	5.58	S−O	5.48	5.5	5.6
O−O	5.63	O−O	5.91		

were well in agreement with each other. As seen in Table 1, the structure of SO_2 molecule in the liquid state does not differ significantly from that in the gaseous and in the crystalline states. The fits between the experimental and theoretical values are shown by dashed lines in Figs. 2 and 3.

Molecular orientation. Information on molecular orientation between SO_2 molecules in the liquid could be obtained from the analysis of the radial distribution functions in the range $3<r< 6$ Å. In the RDFs there appeared some characteristics such as the small hump (3.2 Å) and the shoulder (5.5 Å) in the X-ray case, and the three peaks (3.5, 4.4 and 5.6 Å) in the neutron case. However, the present RDFs are the sum of each partial radial distribution function (S−S, S−O

(a)

(b)

Fig. 6. Two types of configurations between SO_2 molecules found in the crystal structure of SO_2.[7]

and O−O), and hence the construction of a three-dimensional orientation model between SO_2 molecules would not be expected until the partial RDFs were solved by using the isotopic technique or making another diffraction experiment such as electron diffraction.

Sometimes, the short-range ordering in liquids is similar to that in crystals. In the present study, therefore, we applied the molecular orientation between adjacent SO_2 molecules found in the crystal SO_2 to the analysis of the RDFs. According to the crystal structure of SO_2,[6,7] two types of configurations have been reported as shown in Fig. 6. Their interatomic distances are listed in Table 2 and compared with the positions of the peaks in the RDFs. In Table 2 the small hump at 3.2 Å in the X-ray RDF, which emphasizes the sulfur contribution, corresponds well to the S−O interactions at 3.10−3.25 Å. On the other hand, the O−O interactions at 3.26−3.70 Å, which could be seen in the neutron scattering, again fit well with the peak at 3.50 Å in the neutron RDF. Additionally, the value of 3.50 Å, which is larger than the O−O distance (3.26 Å) in configuration (a), may indicate the presence of both types of orientation in the liquid SO_2. The interatomic distances of other S−O and O−O interactions seem consistent with the peak positions in the RDFs. Thus, configurations (a) and (b) shown in Fig. 6 might become a model of the orientational correlation in the liquid SO_2.

Liquid structure model. The radial distribution functions obtained by both these methods show peaks even at 8−9 Å, indicating that the structure of liquid SO_2 is ordered in the relatively long range. In building up a three-dimensional model of the liquid SO_2, it should be noted that a model
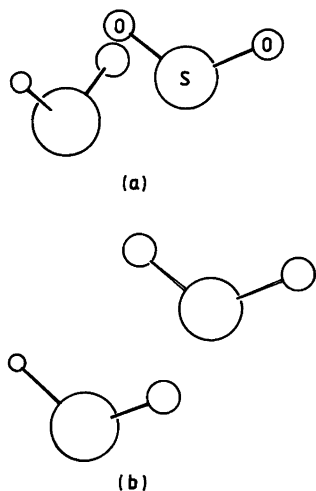
has been deduced from the one-dimensional diffraction data and hence the possibility to explain the data by other models could not be ruled out. In previous studies on molecular liquids such as benzene[18] and carbon tetrachloride,[19] models similar to the corresponding crystal structure or simple bcc or fcc packing arrangements were taken as the ones for their liquid structure. In this sense, we examined two kinds of molecular arrangements; *i.e.* bcc and fcc arrangements of SO_2 molecules. The latter corresponds to the crystal structure of SO_2. In the models both the first and the second neighbour molecules from a central SO_2 molecule were taken into account. The usual agreement factor $R=[\sum k^2\{i(k)_{obs}-i(k)_{mod}\}^2/\sum k^2 i(k)_{obs}^2]^{\frac{1}{2}}$ was used to choose the most likely model for the liquid structure. The comparison k-ranges used in the calculations were $2.0<k<16$ Å^{-1} and $2.0<k<9.7$ Å^{-1} for the X-ray and neutron cases, respectively.

As indicated in the neutron RDF, we assumed the two types of configurations to be present with equal amounts. All the interatomic distances were fixed to the weighted average values found in the crystal structure in the calculations. The rms variations were treated as adjustable parameters. Table 3 gives the parameter values obtained. The fcc model gave the R-value of 0.189 (X-ray) and 0.219 (neutron), while the R-values obtained in the bcc model were 0.170 (X-ray) and 0.163 (neutron). Thus, the bcc cluster model is preferred for the liquid structure of SO_2. In order to test the bcc model without the orientational correlation, another calculation was

carried out with the molecular form factor $f_{SO_2}=f_S+2f_O\sin(kr_{S-O})/(kr_{S-O})$. This model gave the R-value of 0.290, the result indicating the presence of the specific orientational correlation between neighbouring SO_2 molecules in the liquid. The theoretical structure functions calculated using the values given in Table 3 are plotted in Figs. 2 and 3 and agree satisfactorily with the experimental ones. The corresponding RDFs are also shown in Figs. 4 and 5. The peak shapes in the range 3–6 Å are well reproduced. The present bcc cluster model seems likely for the liquid structure of SO_2, but, again we could not rule out the possibility that other models might explain the one-dimensional diffraction data. Recently, the computer simulation (molecular dynamics and Monte Carlo) methods have become one of the powerful means in investigation of liquids.[20,21] In order to further examine the structure and the properties of liquid SO_2, we shall carry out the molecular dynamics calculation which gives us instantaneous three-dimensional structure of the liquid.

Table 3. Parameter values used in the calculations of the theoretical structure functions based on the bcc cluster model. The rms values were adjusted by the least-squares fits. The units on r and l are in Å.

	r	l, X-ray	l, neutron	n
S–O	3.18	0.31	0.50	32
O–O	3.26	0.29	0.30	32
O–O	3.70	0.24	0.24	16
S–S	4.25	0.40	0.29	32
O–O	4.27	0.46	0.37	32
S–O	4.50	0.43	0.38	64
S–O	5.50	0.39	0.48	32
O–O	5.60	0.37	0.50	32

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