An Electron Diffraction Investigation on the Molecular Structures of Sulfur Monochloride and Monobromide

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In 1934 Penney and Sutherland[1] predicted the so-called right-angle model for the molecular structure of hydrogen peroxide on the basis that lone-pair electrons of oxygen atoms hinder the rotation about the oxygen to oxygen axis. Giguère and his collaborators[2] studied the structure of the molecule by various methods and confirmed the prediction of Penney and Sutherland. The molecules of this type are of interest, because they are so simple that precise treatment can be applied to get information on internal rotation. Sulfur monohalide, S_2X_2, belongs probably to the same category. Many researches were carried out on the structure of sulfur monochloride. Morino and Mizushima[3] rejected either the $S{=}SCl_2$ structure or the *trans* configuration by measuring both the dipole moment and the Raman effect, but they did not distinguish between the two possibilities of the right-angle model and of freely rotating one. Gerding and Westrik[4] observed the depolarization degree of the Raman lines in the liquid state. They considered the depolarized line at 106 cm^{-1} as one of the fundamentals, which rejected the C_2 model and preferred the C_{2v} structure (the *cis* form). Some progress in the assignment of an infrared spectrum was made by Bernstein and Powling[5], who resolved the line centered at 440 cm^{-1} into two lines of 438 cm^{-1} and 448 cm^{-1} and found that the spectral data were not inconsistent with a C_2 structure if the line at 106 cm^{-1} in the Raman spectrum was taken as weakly polarized rather than as depolarized and was considered to be due to the torsional oscillation. Recently Luft and Todhunter[6] proposed an idea to interpret the line at 106 cm^{-1} as the first overtone of the torsional mode. It can be expected that the mean square amplitude of a pair of chlorine atoms, if measured accurately, will make a choice between them, because the mean amplitude depends strongly upon the frequency of the torsional mode. The S-S stretching mode has been assigned to one of the two lines resolved by Bernstein and Powling, but when the spectrum of sulfur monochloride is compared with those of monobromide and of monofluoride, it is clear that this assignment is by no means final.

Ackermann and Mayer[7] and Palmer[8] studied the molecular structure of sulfur monochloride by the visual method of electron diffraction, but they did not obtain any precise information about internal rotation. Guthrie[9] arrived by electron diffraction measurement at the result that this molecule has the *cis* configuration, but no precise report has been published. As for physico-chemical investigation on sulfur monobromide, we have only two reports of the Raman effect by Stammreich et al[10,11].

In this paper there is described the result of electron diffraction investigation by the sector-microphotometer method, mainly to see whether the configuration of these molecules is really of the right-angle form or not, and further to determine the potential barrier restricting the internal rotation.

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[1] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.* **2**, 492 (1934).

[2] L. R. Zumwalt and P. A. Giguère, ibid., **9**, 458 (1941); P. A. Giguère, ibid., **18**, 88 (1950); P. A. Giguère and O. Bain, *J. Phys. Chem.* **56**, 340 (1952); P. A. Giguère, I. D. Liu, J. S. Dugdale, and J. A. Morrison, *Can. J. Chem.* **32**, 117 (1954); O. Bain and P. A. Giguère, ibid., **33**, 527 (1955).

[3] Y. Morino and S. Mizushima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **32**, 220 (1937).

[4] H. Gerding and R. Westrik, *Rec. trav. chim. Pays-bas*, **60**, 702 (1941).

[5] H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950).

[6] N. W. Luft and K. H. Todhunter, ibid., **21**, 2225 (1953).

[7] P. G. Ackermann and J. E. Mayer, ibid., **4**, 377 (1936).

[8] K. J. Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938).

[9] G. B. Guthrie, quoted by P. W. Allen and L. E. Sutton, *Acta Cryst.* **3**, 46 (1950).

[10] H. Stammreich, R. Forneris and K. Sone, *J. Chem. Phys.*, **23**, 972 (1955).

[11] H. Stammreich and R. Forneris, *Spectrochim. Acta* **8**, 46 (1956).

TABLE I

EXPERIMENTAL CONDITIONS

Compound	Camera length (cm.)	Wave length of the electron beam (Å)	Sector	Stopper	Index of resolution	Measured range of q value
S_2Cl_2	11.82	0.057	r^2	without	0.73	15-83
	27.91	0.069	r^2	without	0.73	5-27
S_2Br_2	11.82	0.057	r^3	with	about 1	18-95
	27.91	0.056	r^2	with	about 1	6-31

Experimental

Sulfur monochloride obtained from a commercial source was purified by vacuum distillation over dry purified sulfur and activated charcoal. Sulfur monobromide was synthesized from equimolar mixture of purified sulfur and bromine according to the method described by Brauer[12].

The apparatus of electron diffraction and the procedure taken are the same as those previously reported[13]. Two kinds of sector, r^2 and r^3 type, were used. In addition to the of a camera shorter length (11.82 cm.), a longer one with 27.91 cm. length was also used, which was particularly suitable for the study of internal rotation. The experimental conditions are given in Table I.

Analysis

a) Modified Radial Distribution Function.—*Sulfur Monochloride.*—According to the procedure developed by Karle and Karle[14] the molecular intensity curves $sM(s)$ were obtained as shown in Fig. 1.

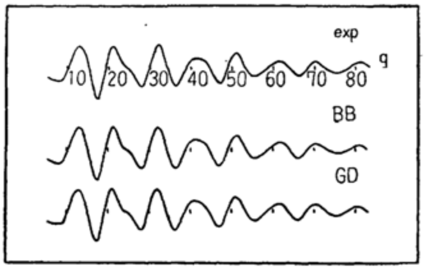

Fig. 1. The molecular intensity curves for sulfur monochloride.

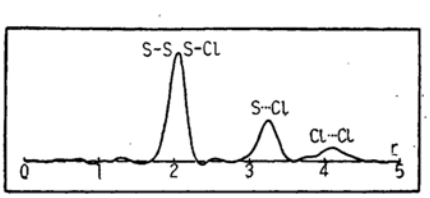

Fig. 2. The modified radial distribution curve for sulfur monochloride.

The radial distribution curve was obtained by Fourier transformation of the molecular intensity curve, in which the intensity from $q=0$ to $q_{\min}$ was spliced by a curve calculated for an assumed model. The curve thus obtained (Fig. 2) consists of three peaks: (S-S, S-Cl), (S···Cl)*, and (Cl···Cl). Although the radial distribution function of the Cl···Cl pair reflects directly the behavior of the internal rotation, it is influenced strongly by the intensity at small q region; when the modified radial distribution function is calculated by supplementing the observed intensity from $q=0$ to 18 with the intensity of the right-angle model or that of the *trans* one, quite different curves are obtained for the Cl···Cl region as seen in Fig. 3.

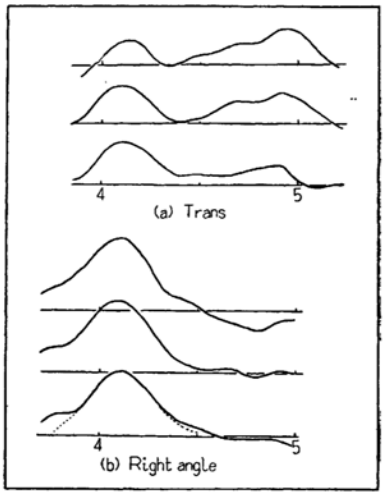

Fig. 3. The modified radial distribution curve for Cl···Cl pair of sulfur monochloride.
(a) interation started from the *trans* form;
(b) it started from the right angle model.

Of course the Fourier transformation must be repeated until the resultant radial distribution function becomes consistent with the assumed model. If the

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[12] G. Brauer, "Handbuch der präparativen anorganischen Chemie" Ferdinand Enke Verlag, Stuttgart (1954), p. 290. See also O. Ruff and G. Winterfeld, *Ber.* **36**, 2437 (1903).

[13] Y. Morino and E. Hirota, *J. Chem. Phys.* (in press).

[14] J. Karle and I. L. Karle, ibid., **18**, 957 (1950).

* S-Cl denotes the directly bonded sulfur-chlorine atom pair and S···Cl the non-bonded atom pair separated by another sulfur atom.

trans model is first assumed, the rate of convergence is quite slow, and the shape of the third peak (Fig. 3a) is different from that of the pure *trans* form and rather like that of the right-angle model with a wide amplitude of torsional oscillation. Under the assumption of the right-angle model a consistent model is readily obtained (Fig. 3b).

The first (S-S, S-Cl) and the second peak (S···Cl) are independent of the assumption about the internal rotation, and hence one can easily get parameters for these atom pairs. However, a difficulty remains in separating two atom pairs, S-S and S-Cl, because these two peaks overlap each other heavily. As shown in Fig. 4 and in Table II, any of three distinct sets of parameters can explain the observed curve equally well. There was no difficulty about the analysis of S···Cl. The results of analysis of the modified radial distribution curve are summarized in Table II, where the peak of Cl···Cl was also assumed to be Gaussian.

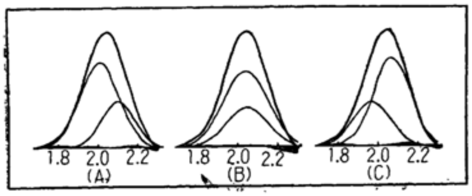

Fig. 4. The compound modified radial distribution curves of S-S and S-Cl pairs of sulfur monochloride, explained by three distinct sets of parameters. (Cf. Table II)

TABLE II

RESULTS OF ANALYSIS OF MRD FOR S_2Cl_2*

	A		B		C	
	r	$\langle \Delta r^2 \rangle^{1/2}$	r	$\langle \Delta r^2 \rangle^{1/2}$	r	$\langle \Delta r^2 \rangle^{1/2}$
S–Cl	2.01	0.06	2.04	0.08	2.07	0.05
S–S	2.10	0.03	2.04_5	0.06_5	1.97	0.05
S···Cl			3.24_5	0.08_7		
Cl···Cl			4.10_7	0.12_5–0.15_5		

* The first number denotes the equilibrium distance and the second the rms amplitude of vibration.

The unmodified radial distribution function[13] may be useful to resolve further this compound peak of S-S and S-Cl, but the error included in the present experiment did not allow any higher resolution. (Compare the reliability factor[13] given in the later section).

Sulfur Monobromide.—As described above it was difficult to obtain accurate values of the S-S and the S-Cl bond distance in a sulfur monochloride molecule. It seems that the length of S-S can be obtained from the analysis of the curve of sulfur monobromide. The modified radial distribution curve is shown in Fig. 6. For calculating this curve, the observed molecular intensity at q larger than 8 (Fig. 5) was corrected for the effect of diffraction by electron cloud[15] and was spliced with the theoretically calculated one in the region from $q=0$ to 8. The S-S and the S-Br pair give two distinct peaks: the lower peak, corresponding to S-S, appears at the short-distance side of the higher peak and is clearly separated from that of the latter. The peak of Br···Br is flatter than that of Cl···Cl and shows considerable deviation from the Gaussian shape. About two thirds of the upper part of the S···Br peak stands clearly above the level of the ghost, but its area amounts to only about 75% of the theoretical one. This difference may be explained by assuming a contamination of bromine. Since the vapor pressure of bromine is far greater than that of sulfur monobromide, we can expect that bromine gas which was first included in the sample was removed by pumping off the gas before the exposure, but sulfur

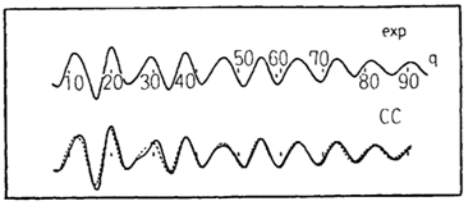

Fig. 5. The molecular intensity curves for sulfur monobromide. The dotted curve is for the case where the bromine is added to about 30%.

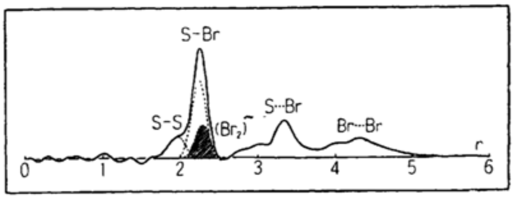

Fig. 6. The modified radial distribution curve for sulfur monobromide. The contamination of bromine is taken into consideration by the shaded area.

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[15] L. S. Bartell, L. O. Brockway and R. H. Schwendeman, ibid., **23**, 1854 (1955).

monobromide is readily decomposed into sulfur and bromine, for example, by radiation of the electron beam or by contact with the metal surface of the apparatus. In fact, if one assumes the mixing of bromine gas, the ratio of areas of S-Br and S···Br peaks can be well explained, because the atomic distance in bromine molecule is about 2.28 Å, comparable with the length of S-Br, so that the presence of bromine vapor will make the area of S-Br pair large. In Fig. 6 the abundance of bromine was tentatively assumed to be about 30%, then the equilibrium distance of S-Br pair must be reduced 0.01 or 0.02 Å from that of the peak (about 2.25 Å). The result of analysis of the modified radial distribution curve is given in Table III.

TABLE III

RESULTS OF ANALYSIS OF MRD FOR S_2Br_2

	r	$\langle \Delta r^2 \rangle^{1/2}$
S-S	~ 1.97	—
S-Br*	2.24	0.05_3**
S···Br	3.35	0.09_3**
Br···Br	~ 4.26	~ 0.31

* When bromine is added, the peak has the parameters $r=2.25$ Å and $\langle \Delta r^2 \rangle^{1/2}=0.04_7$ Å.

** The correction for the Born approximation was carried out by the procedure given in ref. 15.

b) The Correlation Method.—*Sulfur Monochloride.*—It is reasonable to determine first the parameters of S-S and S-Cl by examining the intensity curve in the region of $q \geqq 50$, since the result of analysis of the radial distribution curve showed that the temperature factors of S···Cl and Cl···Cl were definitely large and hence their intensities damped out in this region. Since an atom pair has two parameters to be determined, an equilibrium distance and a temperature factor, four parameters must be taken into consideration. These parameters are strongly dependent on each other, as seen from the three sets given in Table II. The parameter chart of the temperature factor was projected on that of the equilibrium length, the axes of the latter chart being the bond lengths of S-S and S-Cl (Fig. 7). Reasonable models fall on a line connecting three models A, B and C, which were obtained from the analysis of the radial distribution function, whereby temperature factors were taken tentatively for each model. There was found a rough relation between the sum of temperature factors of S-S and S-Cl, M. A., and the difference between their equilibrium distances, Δr:

$$\text{M. A.}=0.15-0.5\,\Delta r,$$

which holds in the range of $\Delta r<0.3$. The atom pair S···Cl influences, in particular, the shape of the maximum at $q=40$ to 45: when the distance is short, the shoulder of the peak at the short-distance side becomes prominent, and the long-distance side falls off rapidly, and when the distance becomes long, the contrary is the case. The best values of this distance are inscribed in Fig. 7 for seven models on the line from A to C. The most satisfactory models are BB and GD, while the model DD is unsatisfactory. The mean amplitude of S···Cl, 0.08_7 Å, is concluded to be reliable within 0.02 Å by the calculation with the model BB.

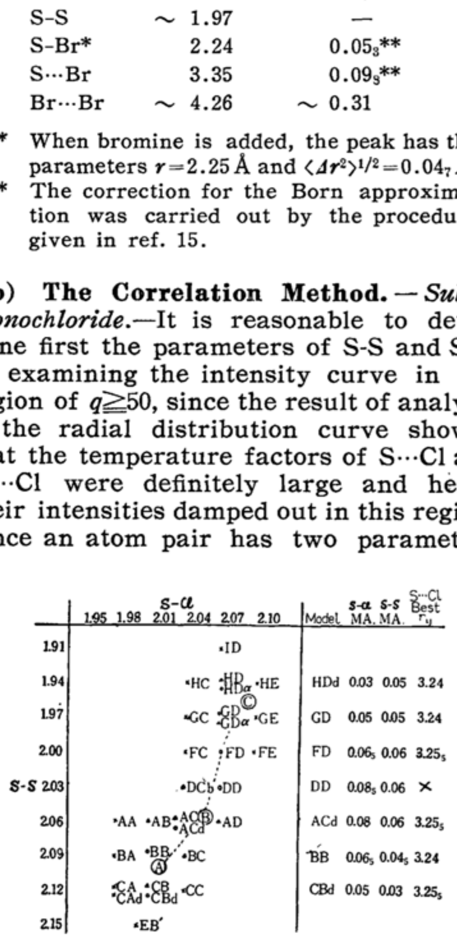

Fig. 7. The parameter chart for sulfur monochloride.

The reliability factors of BB and GD were 10.9% and 10.7%, while the random error of the experiment was 13.2% in the region of $q=18$ to 83. Thus both models agree with the observed intensity within the error. For sulfur monochloride it can not be determined by the analysis which of the models, BB or GD, is better, but the model GD seems to be preferable, for the S-S distance of sulfur monobromide was found to be 1.97 Å. The intensity curves of the models are compared with the experimental one in Fig. 1.

Sulfur Monobromide.—The comparison of the calculated intensity with the observed one was carried out only in the region of $q \geqq 30$, where the intensity of Br···Br was excluded from the calculation, for its amplitude damped out in this region. By taking the length of S-Br to be 2.25 Å two ratios of the atomic distances, (S-S)/(S-Br) and (S···Br)/(S-Br), were varied as the

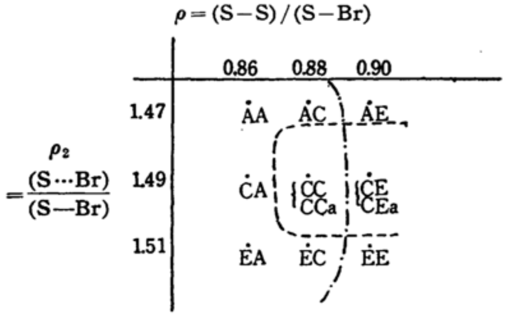

Fig. 8. The parameter chart for sulfur monobromide.

----: acceptable region obtained from the comparison of q_c/q_0

-·-·-: acceptable region concluded from the intensity checking

parameters to be determined. The temperature factors were assumed to be 0.06 Å for S-Br, 0.05 Å for S-S and 0.11 Å for S···Br (these values were mainly taken from the observed values obtained with the radial distribution function, and the correction for the Born approximation was excluded), but later the temperature factor of S-Br was varied and found to be reliable within 0.015 Å. The models were examined referring to the two criteria: the ordinary mean deviation of q_c/q_0 and the amplitude of intensity, the latter being, for simplicity, taken as the intensity from peak to valley; because this definition is free from inadequate drawing of the background line. The parameter chart and the acceptable region are indicated in Fig. 8. The results are:

$$\text{S-Br} = 2.25_9\ \text{Å},$$
$$\text{S-S} = 1.98_8\ \text{Å},$$
and $$\text{S}\cdots\text{Br} = 3.36_3\ \text{Å}.$$

q_c/q_0 of the CC model is 1.004±0.004, and its reliability factor is calculated to be 28.7%, in comparison with the random error of the experiment, 29.4%. The reliability factor can be reduced to 24.9% if it is assumed that the gas contains bromine molecules of 30% in molecular ratio. The dotted line of the model CC in Fig. 5 indicates the effect of bromine mixing. Thus the presence of bromine molecules is again expected in this respect.

The large reliability factor of sulfur monobromide may be explained by the fact that the mixing ratio of bromine gas varied case by case, and the two independent observations did not coincide with each other. In addition to this, the intensity factors of sulfur monobromide are definitely smaller than those of monochloride, owing to the large atomic number of bromine (see Table IV): the ratio of the $sM(s)$ of the two molecules amounts to 2 : 3 or even near 1 : 2.

TABLE IV
INTENSITY FACTORS OF S_2Cl_2 AND S_2Br_2

	S_2Cl_2	S_2Br_2
S-S	72	27
S-X	144	102
S···X	92	70
X···X	39	59

c) Small-Angle Scattering. — *Sulfur Monochloride.*—For further detailed study of internal rotation it is desirable to observe the intensity at a small angle. The principle and the procedure applied were already described in the previous paper[13]. It was the Cl···Cl atom pair to which attention was called. By using the values of parameters: r=2.09 Å, $\langle\Delta r^2\rangle^{1/2}$=0.045 Å for S-S, r=2.01 Å, $\langle\Delta r^2\rangle^{1/2}$=0.065 Å for S-Cl and r=3.24 Å, $\langle\Delta r^2\rangle^{1/2}$=0.09 Å for S···Cl, which correspond approximately to the model A of the modified radial distribution function or to the model BB in the correlation method. The theoretical background functions were calculated for four cases: the *cis*, the *trans*, the freely rotating, and the right-angle configuration**. The curves shown in Fig. 9 clearly indicate that the smoothest one is that of the right-angle model. Thus it can be concluded that the most probable

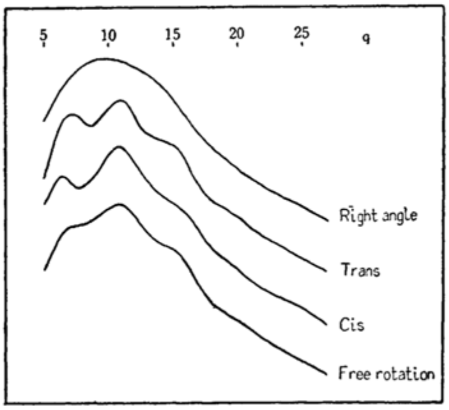

Fig. 9. The background functions for sulfur monochloride.

** The atom form factor used were calculated by Viervoll and Ögrim, *Acta Cryst.*, **2**, 277 (1949) and the inelastic scattering terms were given by Bewilogua, *Physik. Zeits.*, **32**, 743 (1931).

configuration of this molecule is the right-angle type structure.

Sulfur Monobromide.—The background function for S_2Br_2 was calculated by the same procedure: the potential for the internal rotation was taken as $V=\frac{1}{2}V_0(1-\cos 2\phi)$, where three values of $V_0=0$, $4\,kT$ (2.5 kcal/mole), and $8\,kT$ (4.8 kcal/mole) were assumed. A glance at Fig. 10 shows that $V_0=0$ is unsatisfactory in the region of $q=6$ to 13, and V_0 must be larger than $4\,kT$. In the region of $q>13$ none of the three curves are smooth, probably owing to the contamination of bromine. In fact the mixing of bromine molecules of 50% smooths out sufficiently the background function. Thus here is another evidence that the gas was contaminated by bromine, the amounts being 30 to 50%. But the precise value of the potential barrier V_0 could not be obtained because of the contamination of bromine.

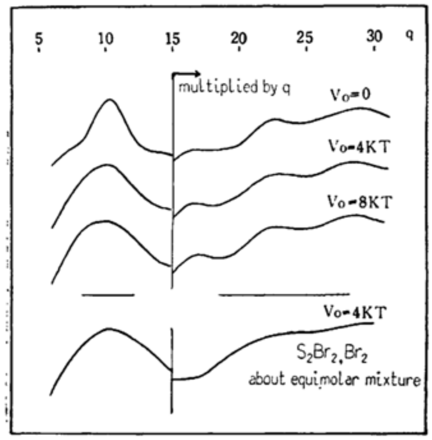

Fig. 10. The background functions for sulfur monobromide.

Calculation of Mean Square Amplitudes

Six fundamental frequencis have been observed for sulfur monochloride by the Raman effect and by the infrared adsorption spectra: their wave numbers are 102, 206, 240, 436, 449, and 540 cm^{-1}.*** According to the assignment given hitherto the lines of 240 and 540 cm^{-1} have been considered to belong to the B class and the other four lines to the A class, but if one compares them with the Raman lines of sulfur monobromide, i. e., with the five lines of 66, 172, 200, 356, and 529 cm^{-1}, then one would recognize that the line 540 cm^{-1} of monochloride and the line 529 cm^{-1} of monobromide are assigned reasonably to the S-S stretching mode. In addition to this, the frequency of the S-S stretching mode of sulfur monofluoride was reported by Barceló and Oteró[16] as 526 cm^{-1}. Thus the correct assignment of sulfur monochloride is taken to be as follows: the four lines, 102, 206, 436 (or 449), and 540 cm^{-1}, belongs to the A type and the remaining two, 240 and 449 (or 436) cm^{-1}, to the B type vibration. Since the measurement of depolarization is very difficult, in particular, for a weak line such as 540 cm^{-1} and for overlapping lines such as 436 or 449 cm^{-1}, the result of the measurement of depolarization can not be considered very serious. In the present type of molecules two S-X stretching modes are likely to have the same frequencies, so that the line 356 cm^{-1} reported for sulfur monobromide included probably the other S-Br stretching vibration just as in monochloride. A weak line at 302 cm^{-1}, omitted first and then reported later by Stammreich et al, can be interpreted to be a combination or difference band, or a band due to impurity. The final assignments are given in Tables V and VI for sulfur monochloride and monobromide, respectively.

In order to obtain the force constants, normal coordinate treatment was carried out, based on the Urey-Bradley type of force fields:

$$\begin{aligned}2V={}&K_{SS}(\varDelta R)^2+K_{SX}\{(\varDelta r_1)^2+(\varDelta r_2)^2\}\\&+H_{SSX}\{(r\varDelta\alpha_1)^2+(r\varDelta\alpha_2)^2\}\\&+F_{SX}\{(\varDelta q_1)^2+(\varDelta q_2)^2\}+\varPhi(r\varDelta\phi)^2\\&+2K'_{SS}R\varDelta R+2K'_{SX}(r\varDelta r_1+r\varDelta r_2)\\&+2H'_{SSX}(r^2\varDelta\alpha_1+r^2\varDelta\alpha_2)\\&+2F'_{SX}(q\varDelta q_1+q\varDelta q_2)+2\varPhi' r^2\varDelta\phi,\end{aligned}$$

where R denotes the equilibrium distance of the S-S atom pair, r_1 and r_2 denote those of the S-X atom pairs, q_1 and q_2 those of the S$\cdots$X atom pairs, α_1 and α_1 the equilibrium values of $\angle$S-S-X, and ϕ stands for that of the torsional angle; $\varDelta$ indicates a displacement from the equilibrium value. The equilibrium value of ϕ is assumed to be 90°. Among the five constants K'_{SS}, K'_{SX},

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*** These values were cited from the reference 11; other workers gave essentially the same results.

[16] J. R. Barceló and C. Otero, *Anal. Real. Soc. Españ. Fis. Quim.* **B51**, 223 (1955).

TABLE V

VIBRATIONAL FREQUENCIES AND FORCE CONSTANTS FOR S_2Cl_2

Symmetry	Observed frequency (cm^{-1})	Assignment	Calculated frequencies I (cm^{-1})	Calculated frequencies II (cm^{-1})	Force constant (md/Å)
A	540	ν(S-S)	536	536	$K_{SS}=2.46$
	436	ν(S-Cl)	440	439	$K_{SCl}=1.87$ $H_{SSCl}=0.21$
	206	δ(SSCl)	212	199	$F_{SCl}=0.19$
	102 or 55	torsion	105	56	$\phi=0.065$(I) $=0.016$(II)
B	449	ν(S-Cl)	446	446	$F'_{SCl}=-0.1\,F_{SCl}$
	240	δ(SSCl)	242	242	

TABLE VI

VIBRATIONAL FREQUENCIES AND FORCE CONSTANTS FOR S_2Br_2

Symmetry	Observed frequency (cm^{-1})	Assignment	Calculated frequency (cm^{-1})	Force constant (md/Å)
A	529	ν(S-S)	531	$K_{SS}=2.46$
	356	ν(S-Br)	354	$K_{SBr}=1.56$ $H_{SSBr}=0.15$
	172	δ(SSBr)	174	$F_{SBr}=0.16$
	66	torsion	63.7	$\phi=0.046_3$ $F'_{SBr}=-0.1\,F_{SBr}$
B	356	ν(S-Br)	357	
	200	δ(SSBr)	201	

H'_{SSX}, F'_{SX}, and Φ', there exist four relations to express the balancing of the forces at the equilibrium configuration. Therefore the constants K'_{SS}, K'_{SX}, H'_{SSX}, and Φ' can be expressed as functions of F'_{SX}. In total, the potential function here assumed has six adjustable parameters for six observed frequencies.

For sulfur monochloride two cases were considered, in one of which the line 102 cm^{-1} was taken the fundamental torsional mode (set I) and in the other of which it was taken the first overtone of this mode (set II). Force constants given in Tables V and VI give the frequencies in very satisfactory agreement with the observed data.

It is easy to calculate the rms amplitudes of vibration from this force fields: they are given by the formula[17]

$$\langle \Delta q^2 \rangle = \boldsymbol{kT}\mathbf{AU'F^{-1}UA'} + (h^2/64\pi^2\boldsymbol{kT})(\mu+\mu')$$

where **A** is a matrix which expresses, in terms of the internal coordinates, the displacement of the distance whose mean amplitude is to be calculated, **U** the transformation matrix between the internal and the symmetry coordinates, $\mathbf{F}^{-1}$ the inverse matrix of **F** expressed in the symmetry coordinates, and μ and μ' stand for the reciprocals of the masses of the atoms located at both ends of the distance. The calculated values are compared with the observed in Tables VII and VIII. Agreement is very satisfactory for S-S, S-X, and S···X atom pairs. The rms amplitude of the Cl···Cl pair in sulfur monochloride was observed to be 0.14± 0.07 Å, in close agreement with the calculated value, 0.15_8 Å, which was based upon the assignment that the line 102 cm^{-1} is the fundamental. For the Br···Br pair of sulfur monobromide such an agreement

TABLE VII

MEAN AMPLITUDES OF S_2Cl_2

	Calculated (Å)	Observed (Å) A	Observed (Å) C
S-Cl	0.054	0.06±0.01	0.05±0.01
S-S	0.048	0.03±0.03	0.05±0.03
S···Cl	0.087	0.08_7 ± 0.02	
Cl···Cl			
(I)	0.158	0.14 ± 0.07	
(II)	0.257		

TABLE VIII

MEAN AMPLITUDES OF S_2Br_2

	Calculated (Å) 25°C	Calculated (Å) 100°C	Observed (Å)
S-Br	0.055	0.060	0.05_3±0.015*
S-S	0.048	0.051	0.05(ass.)
S···Br	0.092	0.101	0.09_8±0.02*
Br···Br	0.189	0.211	~0.31

* Corrected for the Born approximation. (See ref. 15).

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[17] Y. Morino, K. Kuchitsu, and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952); Y. Morino, K. Kuchitsu, A. Takahashi, and K. Maeda, ibid., **21**, 1927 (1953); Y. Morino and E. Hirota, ibid., **23**, 737 (1955).

was not obtained: a rough estimate of the rms amplitude of the Br···Br atom pair gave 0.31 Å, definitely larger than the calculated value of 0.19 to 0.21 Å. This disagreement could be understood by taking into consideration the mixing of bromine discussed above.

The correction for the Born approximation was carried out for S-Br and S···Br atom pairs, by using an approximate formula proposed by Bartell et al.[15].

It may be noted that, if the calculated rms amplitude of S-S and S-Cl are added, they amount to about 0.10 Å. This sum gives, with the relation derived in IIIb, the following two sets of parameters for S-S and S-Cl atom pairs on a line Å to C in Fig. 7 (a) if $r_{\text{SCl}}-r_{\text{SS}}=0.10$ Å, then $r_{\text{SCl}}=2.07$ Å and $r_{\text{SS}}=1.97$ Å, and (b) if $r_{\text{SS}}-r_{\text{SCl}}=0.10$ Å, then $r_{\text{SCl}}=2.00$ Å and $r_{\text{SS}}=2.10$ Å. The set (a) corresponds to the model GD and the set (b) approximately to the model BB.

Discussion

The four distances observed for sulfur monochloride indicate clearly that this molecule does not have the thionyl chloride type structure; because in the latter the length of the Cl···Cl pair must be shorter than 2(S-Cl) sin α (α equals to the angle of S-S-Cl). The observed values of the three atom pairs, S-S, S-Cl and S···Cl, give 3.96 Å for 2(S-Cl) sin α. It is significantly shorter than the observed 4.11 Å, and the discrepancy is definitely beyond the experimental error. Thionyl chloride has a pyramidal structure in which the two OSCl planes are not coplanar, hence in this structure Cl···Cl atom pair would have to be further shorter than 3.96 Å. This holds also for sulfur monobromide: 2(S-Br) sin α (α equals to the angle of S-S-Br) is calculated to be 4.33 Å, which is comparable in magnitude with the observed 4.26 Å, but a definitely shorter distance than 4.33 Å must be given for Br···Br distance of the presumed thionyl chloride type structure. Thus it is concluded that both molecules have the structure containing S-S bond, and the angles of the internal rotation ϕ (the angle between two SSX planes, the position of $\phi=0$ being at the *cis* one) are nearly equal to 90°: precisely speaking, 82.5° for S_2Cl_2, and 83.5° for S_2Br_2.

The bond length of S-S was found to be 1.97 to 1.98 Å from the data of sulfur monobromide, which is somewhat shorter than the usual single bond distance, such as 2.05 Å in H_2S_2[18], 2.05_3 Å in $(CF_3)_2S_2$[19], 2.06_5 Å in $(CF_3)_2S_3$[20], or 2.04 Å in $(CH_3)_2S_2$[20], but longer than the double bond 1.89 Å in S_2[21]. It is to be noted that the S-S stretching modes of sulfur monohalides are about 530 cm^{-1}, higher by about 20 cm^{-1} than those of usual single S-S bond. The length of S-Cl of sulfur monochloride, 2.07 Å is close to S-Cl=2.07 Å in thionyl chloride, but longer than S-Cl=2.01 Å in SCl_2. The frequencies of S-Cl stretching modes in SCl_2 were observed to be 514 cm^{-1} and 534 cm^{-1}, but the corresponding values of sulfur monochloride are 436 cm^{-1} and 449 cm^{-1}. Thus it is likely that there is a parallelism between the vibrational frequencies and the bond lengths. The bond length of S-Br in sulfur monobromide 2.24 Å is also approximately equal to S-Br=2.27 Å in thionyl bromide.

The observed rms amplitude of the Cl···Cl pair of sulfur monochloride indicates that the line 102 cm^{-1} is the fundamental of the torsional oscillation. If the potential energy for this mode, $\frac{1}{2}\Phi(r\Delta\phi)^2$, is set equal to $V=\frac{1}{2}V_0(1-\cos 2\Delta\phi)\cong V_0(\Delta\phi)^2$, then V_0 is found to be about 17 kcal/mole. This potential barrier seems to be high in comparison with that of hydrogen peroxide; for the latter the height of the barrier of 0.3[22] to 4.5[23] kcal/mole was reported. Though the accurate evaluation of the interaction between the lone-pair electrons of oxygen atoms is very difficult, its estimation would be possible by calculating the overlap integral of $p\pi$ electrons. For the O-O bond length of 1.48 Å the overlap integral of $2p\pi$ electrons is 0.069 and for the S-S bond length of 1.97 Å $3p\pi$ electrons have the overlap integral of 0.152. The ratio of squares of these two integrals, which are considered to be a measure of the interaction of $p\pi$ electrons, is about 1 : 4.8. Hence a higher barrier is expected for the sulfur compound, in agreement with the observation. A similar discussion

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18) M. K. Wilson and R. M. Badger, ibid., **17**, 1232 (1949).

19) H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 452 (1954).

20) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

21) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II. D. van Nostrand Co., New York, (1945).

22) J. T. Massey and D. R. Bianco, *J. Chem. Phys.*, **22**, 442 (1954).

23) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, ibid., **17**, 1248 (1949).

for sulfur monobromide was limited by the contamination of bromine.

As mentioned already, the rms amplitude of Br···Br was observed considerably larger than the calculated. The reason may be attributed to the anharmonicity of the torsional oscillation. Since the frequency of the torsional mode of sulfur monobromide is 66 cm^{-1}, there must be many molecules in the first, the second, and the third excited torsional state, and all these molecules can make transitions of the torsional oscillation (a kind of hot band), then anharmonicity of this mode would be greater. It is, however, difficult to know the real shape of the potential barrier through the data available at present.

Conclusion

By the sector and microphotometer method the molecular structures of sulfur monochloride and monobromide were obtained as follows:

sulfur monochloride:

S-Cl: $r=2.07\pm0.01$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.05\pm0.01$ Å,

S-S: $r=1.97\pm0.03$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.05\pm0.03$ Å,

S···Cl: $r=3.24_5\pm0.02$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.08_7\pm0.02$ Å,

Cl···Cl: $r=4.11\pm0.05$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.14\pm0.07$ Å,

$\angle$S-S-Cl$=107°\pm2.5°$,
$\phi=82.5°\pm12°$ ($\phi=0$ at the cis).

sulfur monobromide:

S-Br: $r=2.24\pm0.02$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.05\pm0.02$ Å,

S-S: $r=1.98\pm0.04$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.05$ Å (assumed),

S···Br: $r=3.35\pm0.02$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.09_8\pm0.02$ Å,

Br···Br: $r=4.26\pm0.08$ Å,
$\langle\Delta r^2\rangle^{1/2}=0.31$ Å,

$\angle$S-S-Br$=105°\pm3°$,
$\phi=83.5°\pm11°$ ($\phi=0$ at the *cis*).

Both molecules have the right angle structure of hydrogen peroxide type.

The lowest band 102 cm^{-1} of sulfur monochloride was concluded from the observed mean amplitude of Cl···Cl to be the fundamental of the torsional mode, contrary to the proposal by Luft and Todhunter. Sulfur monobromide is easily decomposed, and bromine molecule thus evolved obscured the intensity of sulfur monobromide, but free rotation was definitely denied and torsional oscillation about the right angle position was clearly concluded.

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