be used to lower the energy required to produce the CH_2 ion. If this assumption is made and if consistent values are used for the heat of formation of carbon monoxide and for the C=C and C=O bond energies, then with the above value of 11.9 v. for the ionization potential of CH_2 we calculate for the appearance potential of CH_2^+ from ketene a value of 13.7 electron volts. This result is in excellent agreement with the observed value of 13.8 ± 0.2 v. and argues for the correctness of this energy coupling mechanism. A very similar mechanism of energy coupling has been postulated to explain the low value of the threshold energy for the photochemical dissociation of ketene.[25]

The possibility of such energy coupling mechanisms makes unambiguous interpretation of most appearance potentials of fragments from diketene very difficult. The relatively low value of the appearance potential of ions of mass 56 suggests an energy coupling mechanism of the type described above. In this case neither the structure nor the ionization potential of the product ion is known and so a quantitative treatment of the energetics of the formation of this ion is impossible at present. The difference between the appearance potentials of ketene ion from monomer and dimer is 1.9 ± 0.3 electron volts which corresponds to a heat of formation of dimer from monomer of 44 ± 7 kcal. Actually this value is only an upper limit since fragments from the diketene can conceivably be formed either with excess kinetic energy or in an excited state.

ITHACA, N. Y.
UPTON, LONG ISLAND, N. Y.

(25) R. G. W. Norrish, H. G. Crone and O. Saltmarsh, *J. Chem. Soc.*, 1533 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

An Electron Diffraction Study of Disulfur Decafluoride

BY R. B. HARVEY[1] AND S. H. BAUER

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An electron diffraction study has been carried out on the compound disulfur decafluoride. The compound was prepared by the passage of fluorine over sulfur as reported by other investigators. Electron diffraction photographs were taken with and without the use of a rotating sector, and the photographic intensity curve was inverted to a radial nuclear charge density distribution curve by IBM computing methods. Some information on the vibrational displacements of the atomic pairs in the molecule was obtained from the radial distribution curve. A molecular model was proposed in which two octahedral (SF_5) groups are joined by a sulfur–sulfur bond. The sulfur–fluorine distance is 1.56 ± 0.02 Å. and the sulfur–sulfur distance is 2.21 ± 0.03 Å. The (SF_5) groups exhibit hindered rotation about the sulfur–sulfur link as axis.

Introduction

Fluorine is the only halogen with which sulfur forms a saturated hexacoördinated molecule SF_6, a compound that is unique in its stability and chemical inertness. The compound disulfur decafluoride was prepared by Denbigh and Whytlaw-Gray[2] who measured many of its physical and chemical properties and, on a basis of the parachor and the general chemical similarity to SF_6, suggested that it contained a sulfur–sulfur bond linking two (SF_5) groups. Recently Hollies and McIntosh[3] prepared the compound again and made a careful determination of the properties, in particular the dielectric constant. They concluded that disulfur decafluoride is a highly stable, non-polar dielectric and they also suggested that a reasonable configuration might be two sulfur atoms linked together, each surrounded by five fluorine atoms, covalently linked.

Although these workers have both proposed a sulfur–sulfur link in the molecule, the possibility of a fluorine bridge between the sulfur atoms is not definitely excluded.

This structure is open to several objections; whereas it has been demonstrated that other halogen atoms form stable bridges of the type indicated, the existence of such a bridge involving fluorine atoms has not been demonstrated although some investigators have proposed it. In the above structure if each of the bonding fluorine atoms contributes 3 electrons toward bonding, each of the sulfur atoms would be left with an unpaired s-p-d hybridized electron; then the molecule should exhibit a magnetic moment.

In view of the evidence of the parachor and the dielectric constant as mentioned above, the low boiling point of disulfur decafluoride (29°), and its general inertness to chemicals, molecular configurations with less symmetry than those proposed above were discarded. An electron diffraction study on the vapor was carried out to obtain information on bond distances and to establish the correctness of the model first suggested.

Experimental Procedure

The S_2F_{10} used in this study was prepared by the passage of gaseous fluorine over solid sulfur as described by several authors.[2-5] The chief product is SF_6; the $(SF_6 + S_2F_{10})$ fraction can be separated from other products by virtue of its chemical inertness; and finally a low temperature distillation serves to separate the SF_6 from the S_2F_{10}. Redistillations at low temperature *in vacuo* were used to purify the S_2F_{10} fraction; vapor density measurements were used as a criterion of purity. Because of the high molecular weight of S_2F_{10} (254.1) the vapor density method was a sensitive measure for small amounts of SF_6 impurities.

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(1) Suffield Experimental Station, Ralston, P. O., Alberta, Canada.

(2) K. G. Denbigh and R. Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934).

(3) N. R. S. Hollies and R. L. McIntosh, *Can. J. Chem.*, **29**, 494 (1951).

(4) D. M. Yost, "Inorganic Syntheses," Vol. I, John Wiley and Sons Inc., New York, N. Y., p. 121.

(5) W. C. Schumb, *Ind. Eng. Chem.*, **39**, 421 (1947).

The apparatus and electron diffraction procedures are described in detail in a paper by Hastings and Bauer.[6] Samples of the gas for diffraction were transferred to a bulb and the required pressure was obtained by surrounding the bulb with a Dry Ice and acetone-bath adjusted to the proper temperature. Approximately 45–47 mm. pressure was obtained with a bath temperature of −30°. Electron diffraction pictures were taken with and without the use of a rotating sector.

A "visual" intensity curve was drawn from estimations of the diameters and densities of the rings of the non-sector photographs. The values for q_0 and I are shown in columns 3 and 4 of Table I. Microphotometer tracings were made of sector photographs and the q_0 and I values are given in columns 5 and 6 of Table I. A composite curve of intensity *vs.* q was then drawn using (1) a computed curve for a model, which from initial trials appears to be quite satisfactory, for the region $q = 0$ to $q = 10$ or 12, over which both visual and microphotometer observations are uncertain; (2) microphotometer intensity values from $q = 10$ (the end of the computed curve) to $q = 70$, and visual values of peak or valley positions in a few cases where the microphotometer values of position were less certain due to graininess or uncertainty of the maximum or minimum point; and (3) visual estimates both of position and intensity from $q = 70$ to $q = 95$. This curve now represents the observed data given under "Final values," columns 7 and 8 of Table I.

TABLE I

OBSERVED INTENSITY DATA FOR ELECTRON DIFFRACTION PHOTOGRAPHS

		Visually estimated			Microphotometer intensities (relative to unit background)	Final values	
Max.	Min.	q_0 (non-sector)	Intensity	q_0 (sector)		q_0	Intensity
1		..	....	..	.....	..	....
	1	7.3	− 9	8	−0.137	7.1	− 4
2		11.3	+ 9	10	+ .158	11.5	+ 4.5
	2	14.1	−10	14	− .325	13.5	− 9.5
3		16.5	+10	16.6	+ .478	16.5	+14
Shoulder		18.4	+ 4	21.1	− .256	21.1	− 7.5
	3	24.0	− 6	23.5	− .523	23.6	−15
4		29.9	+16	30.3	+ .467	30.2	+14
	4	35.6	− 8	35.3	− .380	35.5	−11
5		39.4	+12	40.4	+ .228	40.0	+ 6.5
	5	42.8	− 3	43.2	− .051	43.0	− 1.5
6		46.0	+ 4	46.2	+ .05	46.0	+ 1.5
	6	51.0	− 6.5	49.9	− .084	49.9	− 2.5
7		56.2	+ 7	56.3	+ .126	56.2	+ 3.5
Shoulder		58.7	+ 2.5	59.3	+ .047	59.3	+ 1.5
	7	61.3	− 5.5	62.6	− .100	61.3	− 3
8		66.8	+ 5.5	67.7	+ .111	67.2	+ 3.5
	8	70.8	− 3			70.8	− 3
9		74.9	+ 0.75			74.9	+ 1
	9	78.2	− 1			78.2	− 1
10		81.7	+ 1.5			81.7	+ 2
	10	87.5	− 1.5			87.5	− 1
11		93.0	+ 1			93.0	+ 1

Analysis of Data

(1) **Method.**—The analysis of the data follows the general procedure of a fourier inversion of the intensity pattern to a radial nuclear charge density distribution function, which is then decomposed into the atomic spacings.[7] These must be found with the correct weights in any proposed model of the molecule. A model is chosen on a basis of the best fit of the interatomic distances with those obtained from the radial distribution curve, and confirmation of the model is obtained by a comparison of computed and observed intensity curves.

The inversion of the observed intensity curve follows the procedures of Bauer and Coffin.[8] They multiply the observed curve by an average atom form factor and so derive a curve equivalent to that which would be observed if the scattering were purely nuclear. Essentially this consists of adjusting the curve so that the atom factors f_i, f_j and g_i are properly replaced by the atomic numbers Z_i, Z_j and Z_i, respectively, the limiting values of the form factors at large scattering angles. The calculation was carried out by punched card procedures with IBM calculators, the actual inversion being a step summation which is equivalent to

$$2\pi^2 r \underline{D}^*_{\mathrm{m}}(r) \cong \int_0^{q\ \mathrm{max}} [s\underline{J}_{\mathrm{m}}(s)]_{\mathrm{composite}} \exp\,[-\gamma^2 s^2] \sin rs\, \mathrm{d}s, \qquad \text{where } s = ((\pi/10)q)$$

and $\underline{D}^*_{\mathrm{m}}(r)$ is the charge distribution function corresponding to an intensity curve for nuclear scattering $\underline{J}_{\mathrm{m}}((\pi/10)q)$ over the range 0 to q_{max} modified by an additional temperature factor exp $[-\gamma^2 s^2]$. The parameter γ was adjusted so that $\exp\,[-(\pi^2\gamma^2/100)q^2] = 0.1$ at q_{max} $[q_0 = 10s/\pi]$.

The section of the curve from $q = 0$ to $q = 10$ or 12, was calculated for the selected model by the formula

$$\underline{J}_{\mathrm{m}}((\pi/10)q) = \sum_{\mathrm{ij}}{}' Z_{\mathrm{i}}Z_{\mathrm{j}} \exp\,[-\alpha^2_{\mathrm{ij}}((\pi/10)q)^2] \frac{\sin r^0_{\mathrm{ij}}((\pi/10)q)}{r^0_{\mathrm{ij}}((\pi/10)q)}$$

where r^0_{ij} is the equilibrium separation of the atom pairs, and $\underline{J}_{\mathrm{m}}((\pi/10)\ q)$ is the intensity of nuclear scattering.

(2) **Radial Distribution Curve and Identification of Molecular Spacings.**—The intensity curve[9] was prepared in the manner described and inverted. The heights of the peaks and their areas yield information on the atomic numbers and temperature factors of the atom pairs concerned, and by decomposing the radial distribution envelope into the component peaks it is ideally possible to determine the inter-atom distances and their temperature factors.

The derived radial distribution envelope and the component peaks obtained by analysis are shown in Fig. 1. The large peak at 1.56 Å. is symmetrical about a center line at 1.556 Å. and the uncertainty in this distance appears to be less than 0.01 Å., especially as this peak is the contribution from one spacing only in the molecule. The distance is identified with the (S–F) bond previously reported by Pauling and Brockway,[10] and others.[11,12]

The (F–F) distance is 2.20 Å. when the (S–F) bond is 1.55_6 Å. for an octahedral sulfur atom. The peak close to 2.20 Å. is again very symmetrical about a center line (2.20_4 Å.) and may be assigned principally to (F–F) spacings within the SF_6 group. Two further spacings contribute to this peak, namely, the (S–S) bond, and the (F–F) spacing of fluorine

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[6] J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).

[7] F. A. Keidel, Ph.D. thesis, Dept. of Chem., Cornell University, 1951. (The method used for the treatment of the data is described in detail.)

[8] K. P. Coffin, Ph.D. thesis, Dept. of Chem., Cornell University, 1951.

[9] The composite intensity curve is shown in Fig. 4 and labeled "OBS."

[10] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 68 (1933).

[11] H. Baune and S. Knoke, *Z. physik. Chem.*, **B21**, 297 (1933).

[12] D. P. Stevenson and H. Russel, Jr., THIS JOURNAL, **61**, 3264 (1939).

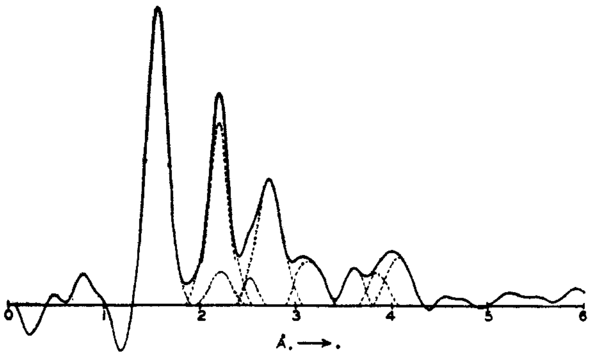
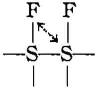
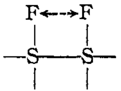
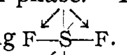


Fig. 1.—Radial charge density distribution curve for S_2F_{10} calculated from the intensity curve by the method of Bauer and Coffin. The envelope of the curve is broken down into separate probability peaks. Contributions between 0–1 Å. are considered spurious, as are certain of the contributions beyond 4.5 Å.

atoms in opposing SF_5 groups when free rotation is assumed. This question will be considered in detail later.

The next two peaks (2.72 and 3.08 Å.) blend together. Separating them gives bell-shaped curves at about 2.72 and 3.12 Å. The left side of the 2.72 Å. curve has a pronounced shoulder which may be reduced to a smaller contribution at 2.52 Å. The peak at 2.72 Å. is the contribution from the spacing  and the peak at 2.52 Å. from the spacing  when the 4 fluorine atoms of one sulfur are interlocked with the 4 fluorine atoms of the other sulfur at 45° out of phase. The peak at 3.12 Å. occurs from the spacing .

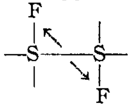
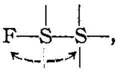
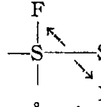
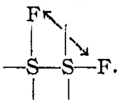
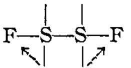
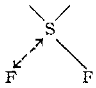
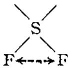
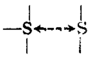
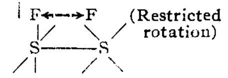
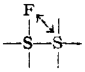
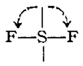
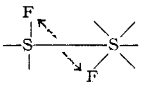
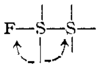
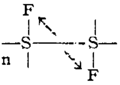
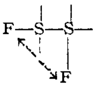
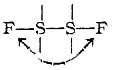
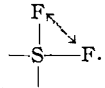
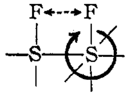
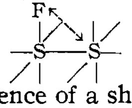
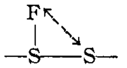
The next peak is at 3.62 Å. and overlaps into the large composite peak at 4 Å. Analysis of this double peak suggests three spacings: (a) 3.62 Å. due to the  separation for the interlocked position of completely restricted rotation; (b) 3.84 Å. which is near the spacing (3.80 Å.) for , and the spacing  (3.82 Å.) for free rotation; (c) 4.08 Å. from the spacing . The small broad peak at 5.24 Å. is probably due to the  spacing, but a contribution at 4.5 to 4.6 Å. and another near 6 Å. cannot be identified with any spacings in the molecular model proposed. A summary of the interatomic spacings and their identification with the features of the radial distribution curve is given in Table II.

TABLE II

COMPARISON OF OBSERVED INTERATOMIC SPACINGS WITH THOSE OF THE MOLECULAR MODEL

Radial distribution maximum, Å.	Relative intensity	Identification of interatomic spacing in molecule	Distance in best model, Å.	Weight
1.55_6	3.5		1.55_6	1440
2.20			2.20_6	1296
2.20	0.5		2.22	256
2.50	0.5	 (Restricted rotation)	2.52	324 (max.)
2.72	3		2.71	1152
3.13	1		3.11	324
3.61	1	 (Restricted rotation)	3.63	324 (max.)
3.84	1		3.76	288
		Free rotation 	3.82	..
4.08	1.5		4.08	648
5.24	0.5		5.33	81

(3) **Quantitative Correlation of Observed Peaks with a Model.**—An examination of the first three peaks suggests fairly narrow limits on the molecular parameters. The symmetry of the peak at 1.55_6 Å. about the center line suggests it to be highly unlikely that the spacing falls outside the range 1.55–1.56 Å. The next peak (2.20 Å.) is symmetrical about points that may vary from 2.200 to 2.204 Å. This peak can have contributions from 3 spacings: (i) The (F–F) link: . This distance is dependent on the (S–F) distance and may vary from 2.192 Å. when (S–F) is 1.550 Å., to 2.206 Å. when (S–F) is 1.560 Å. (ii) The (S–S) link: This link determines the separation between (SF_5) groups and is one of the chief structural parameters. Its minimum value is determined by the van der Waals radius of the peripheral fluorine atoms on opposing (SF_5) groups. (iii) An (F–F) spacing between fluorine atoms of opposite (SF_5) groups when completely free rotation is assumed.  rotation about the (S–S) axis.

The third peak  occurs at 2.72 Å. and although the presence of a shoulder on the left side distorts its appearance, the peak maximum is quite sharp. Drawing the left hand side of the peak to match the right hand side makes the peak symmetrical about a center line at 2.717 Å., and allows the shoulder on the left hand side to be resolved into a smaller peak in the region of 2.5 Å. Identification of the 2.71_7 Å. peak with the separation  $-\overset{\overset{\displaystyle F}{|}}{S}-S-$ leads to a value close to 2.20 Å. for the (S–S) link. Whether any appreciable difference in shape and height of the peak at 2.20 Å. of the radial distribution curve is caused by varying the (S–S) bond length, was investigated by synthesizing a series of peaks with a fixed (F–F) distance of 2.20 Å. and various (S–S) distances from 2.18–2.24 Å. Using these three peaks as criteria we find that the radial distribution curve requires molecular models to have parameters falling within the limits: (S–F) bond 1.55 to 1.56 Å.; (S–S) bond 2.18 to 2.24 Å.

To attempt an exact decomposition of the radial distribution curve into component peaks (identified as molecular spacings) as regards both position and area under the peaks introduces some inconsistencies into the molecular model postulated. In a sense this is a measure of the self consistency of the intensity data. The area under any bell-shaped peak is proportional to (nZ_iZ_j/r_{ij}^0) where nZ_iZ_j is proportional to the scattering power of the atom pairs and r_{ij}^0 is the equilibrium spacing. A comparison of measured and computed areas for the peaks reveals the following (see also Table III): (a) The area of the peak at 3.12 Å. is too great by almost 50%. (b) If one elaborates the shoulder on the left hand side of the peak at 2.72 Å. to give a contribution for restricted rotation in line with that at 3.62 Å., it causes the 2.72 Å. peak to be shifted to 2.73–2.74 Å. which is 0.02 to 0.04 Å. too large. A more consistent set of r_{ij}^0 values is obtained by fixing the peak at 2.72 Å. Increasing the area under the 2.52 peak at the expense of that under the 2.72 Å. peak gives both peaks nearly the correct value for the area. (c) The area under the 4.08 Å. peak as drawn is slightly large and reduction of this causes the peak at 3.85 Å. either to be extended and shifted to the right, or a secondary peak to be introduced which appears near 3.96 Å. Neither of these results is in agreement with the proposed model. Actually the peak at 3.85 Å. should be expected to lie nearer 3.80 Å., but to put it in this position affects adversely both the 3.62 Å. peak and the 4.08 Å. peak. (d) The peak at 5.23 Å. should occur nearer 5.30–5.35 Å. The observed peak is slightly misplaced and too shallow. (e) The peak at 0.76 Å. cannot be found in the molecular model proposed, nor can those at 4.56 or 5.92 Å. These latter are minor and their omission in recalculations of intensity should not affect the shape of the intensity curve too greatly.

TABLE III

ANALYSIS OF PROBABILITY PEAKS IN RADIAL DISTRIBUTION CURVE

Peak position	Contributions to peak	nZ_iZ_j r_{ij}^0	Area under peak	Factor = area nZ_iZ_j/r_{ij}^0
1.56 Å.	10(S–F)	926	2003	2.16
2.20	16(F–F) +	706	1443	2.04
	1(S–S) + free rotation			
2.52	60% contribution from	154	386	2.51
	restricted rotation			
2.72	8(S–F)	424	950	2.24
3.12	4(F–F)	104	360	3.46
3.62	8(F–F) +	105	221	2.10
	60% restricted rotation			
3.79	2(S–F)	76	159	2.09
4.08	8(F–F)	159	364	2.29

(4) **Rotation about the S–S Bond.**—The above considerations permit all the distances in the molecule to be fixed except those which are dependent on the rotation of one (SF_6) group relative to the other about the (S–S) bond as an axis. Specifically such rotation affects the 4 fluorines of each (SF_6) off the (S–S) bond axis. Two extremes arise: (i) Completely restricted rotation where the two (SF_5) groups are interlocked; (ii) Completely free rotation where one group spins freely with respect to the other about the S–S bond as an axis.

The interlocked position would give rise to two distinct and fairly strong contributions in the regions of 2.50 and 3.63 Å. (for S–F = 1.56 Å., and S–S = 2.20 Å.). The peak which forms the shoulder of the larger 2.72 Å. peak is the shorter of these distances and the peak at 3.61–3.62 Å. is the longer. Hence the two (SF_5) groups do not revolve in a completely free manner. How completely the rotation is restricted (*i.e.*, how large is the potential barrier to rotation) is more difficult to determine since the maximum and minimum distances for free rotation would fall at 2.20 and 3.83 Å., points that are obscured by larger peaks, and the contributions of completely free rotation are of a nearly continuous nature between 2.2 and 3.8 Å. which tends further to obscure the peaks.

Synthetic radial distributions for a sequence of barriers restricting rotation are shown in Fig. 2. Curve 1 is for one extreme in which rotation is completely restricted (infinite barrier), while curve 7 is at the other, in which rotation is completely free (zero barrier). For completely restricted rotation there are 2 peaks, independent and discrete. For free rotation the peaks are little more than $^1/_3$ the height of those for restricted rotation, and a continuous charge density contribution extends from the minimum atom separation value to the maximum value. Combining these extremes gives rise to the curves labeled 1 through 7 for 0, 20, 40, 60, 80, 90 and 100% "free rotation contribution." Since the general shape of the radial distribution curve does not change rapidly as the contribution from the curve for free rotation increases from 0–50%, one can determine only broadly the degree to which rotation is restricted. Only when the contribution of free rotation is 80–90% of the whole does the peak at the shorter distance become double, and the peak at the longer distance broadens and shifts somewhat to the right.

We may put broad limits on the degree of restriction of the rotation. Completely restricted rotation would put the peak for the shorter distance in the region 2.50–2.54 Å. Appreciable contributions (greater than 60%) from a free rotation model moves the peak to 2.2–2.4 Å. and almost removes its identity. The experimental curve shows a peak in the region of 2.5 Å. with no essential broadening toward 2.4 Å. This suggests that the peak

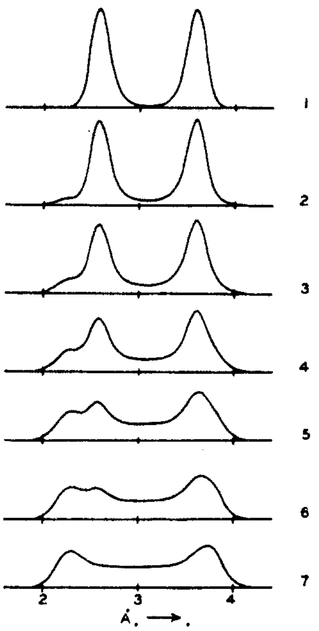


Fig. 2.—Contributions of combinations of free and restricted rotation between (SF_5) groups of the S_2F_{10} molecule to the synthetic radial distribution curve. Curve 1 represents a completely restricted or interlocked molecule, the interlocking fluorine atoms being able, however, to rock slightly. Curve 7 represents a completely free rotation model in which the two (SF_5) groups can spin freely with respect to one another. Curves 2 through 6 represent progressive contributions of free rotation of 20, 40, 60, 80 and 90% to the radial distribution curve.

for the longer distances be at 3.60-3.65 Å.; while contributions from a free rotation model broadens the peak and shifts it toward 3.70 Å. The occurrence of the experimental peak at 3.62 Å. together with a minimum in the experimental curve at 3.73 Å. argues that the rotation is largely restricted. Perhaps the model for free rotation does not make more than a 50% contribution to the radial distribution curve.

In Fig. 3 are shown some synthetic radial distribution curves based on the considerations above. To obtain the radial distribution curve all interatomic distances in the molecule were calculated. A temperature factor was assigned to each distance which, in effect, allows it to vary about its mean value according to a Gaussian probability distribution function. The temperature factors assigned are: $\alpha^2 = 0.0015$ for bonded atom pairs; $\alpha^2 = 0.0023$ for next-to-bonded atom pairs; and $\alpha^2 = 0.0034$ for all other atom pairs in the function $r_{ij} = r^0_{ij}\exp\left[-(r^0_{ij} - r_{ij})^2/4\alpha^2\right]$. The probability loops were calculated to have an area proportional to the scattering power of the atoms concerned, and these were summed to obtain the final radial distribution curve. Models A-1 and A-2 represent, respectively, the synthetic radial distribution curves for the completely free and completely restricted extremes of rotation [(S–F) = 1.55_6 Å. and (S–S) = 2.23 Å.]. The gross differences in the radial distribution curve for restricted rotation from that for free rotation (A-1) are the appearance of a shoulder at 2.5 Å. and the strong contribution at 3.6 Å. Finally Model A-3 is a composite of these two, the restricted rotation model contributing 60% and the free rotation model 40% to the final curve. The shoulder at 2.5 Å. is still apparent, although the peak at 3.6 Å. is no longer dominant. A radial distribution curve for the bridge model has been calculated and included in Fig. 3. The disagreement between it and the "observed" curve at distances greater than 3 Å. is so marked that it must be rejected in favor of the model with a S–S link.

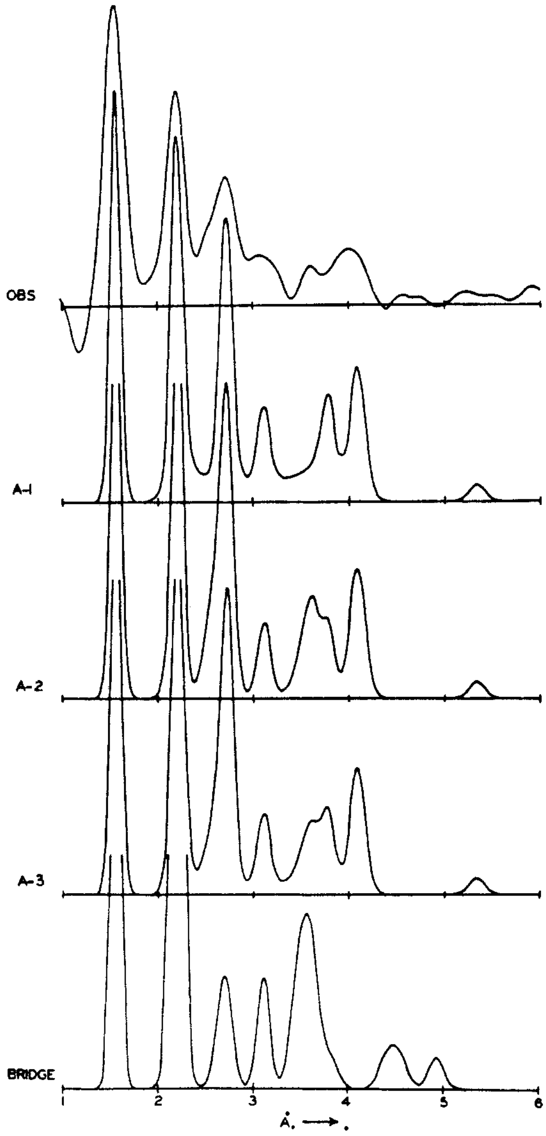
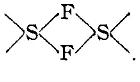


Fig. 3.—Synthetic radial charge density distribution curves for S_2F_{10}. The radial distribution curve computed from the observed intensity curve is plotted at the top. Models A-1, A-2 and A-3 are constructed with two (SF_5) groups joined by an (S–S) link and are, respectively, models with completely free rotation, completely restricted rotation, and with a 40%/60% combination of free and restricted rotation. The bridge model is built up of two (SF_4) groups joined with two fluorine atoms into a 4-membered bridge .

(5) **Vibrational Displacements.**—Karle and Karle,[13] and Keidel[7] have shown that, if the radial distribution curve is decomposed into its component bell-shaped peaks, these may be treated individually to obtain the interatomic vibrational amplitudes. From the bell-shaped peak (usually the upper two-thirds is used to avoid complications with minor variations in the curve) one determines $<l_{ij}^2>_{Av}$ which is the "mean-square amplitude of vibration projected on the line connecting a pair of atoms at equilibrium" (Karle and Karle). Values are given in Table IV below for a number of the peaks of the radial distribution curve for S_2F_{10}. By considering the deviations of the shape of an observed peak from that of an idealized curve one may estimate the standard deviation (expressed as a percentage error). For shorter distances the errors are reasonable but they may be considerable at the longer distances.

TABLE IV

MEAN SQUARE AMPLITUDE OF VIBRATION FOR ATOM PAIRS IN S_2F_{10}

Bond	r_{ij}^0	$<l^2_{ij}>_{Av}^{1/2}$	% error (standard deviation)
S–F	1.56	0.07_5	4
F–F	2.20	.07	2.5
S–F	2.72	.11	5.5
F–F	3.12	$.1_3$	17
F–F	3.62	$.0_8$	10
F–F	4.07	$.1_1$	18.5

When data are exact from which the radial distribution curve is obtained, the method yields values of the root-mean-square projected amplitudes with some accuracy. Although these have been calculated in the table above the values should be considered to be approximate unless supporting evidence, such as spectroscopic measurements, is taken in conjunction with them.

(6) **Comparison of Theoretical and Experimental Intensity Curves.**—In section (3) of this discussion the radial distribution curve was broken down into the atomic spacings which must be found in any proposed model of the molecule. A model was chosen and the interatomic distances of this model were shown to be identifiable with the peak positions of the radial distribution curve. Further confirmation of the correctness of the model proposed as well as a refinement of the parameters can be obtained by a comparison of computed intensity curves with the observed curve.

TABLE V

ATOMIC PARAMETERS FOR A SERIES OF MODELS OF S_2F_{10}

Model	S–F, Å.	S–S, Å.	Remarks
C	1.56	2.16	Rotation completely restricted
D	1.56	2.20	Rotation completely restricted
G	1.56	2.23	Rotation completely restricted
H	1.56	2.23	Rotation completely free
E	1.56	2.20	Rotation completely free
F	1.56	2.20	Curve composed for a 50–50 mean between curves for completely restricted and completely free rotation

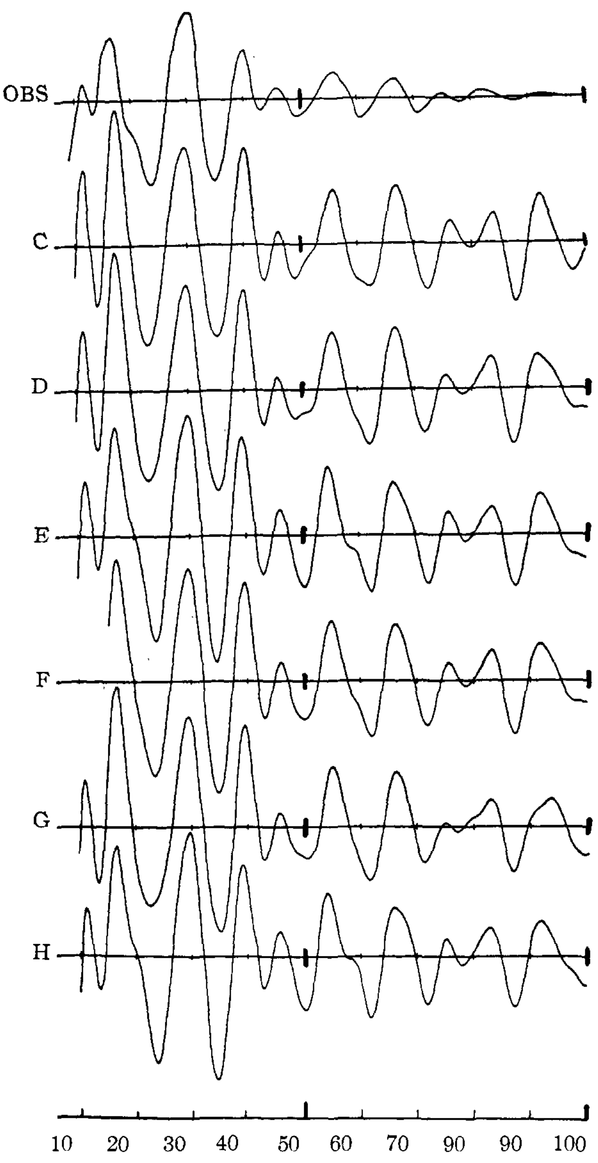


Fig. 4.—Calculated intensity curves for S_2F_{10} computed on an IBM calculator as a function of q ($q = 40/\lambda \sin \theta/2$). See Table V for details of parameters.

In Fig. 4 are drawn the calculated intensity curves for a number of models with parameters as shown below.

When agreement has been obtained between the maxima and the minima there are some small features that are of significance: (a) the shoulder at $q = 20$. This shoulder does not appear in any curve in which the rotation between (SF_5) groups was wholly restricted. It is most prominent when the rotation is quite unrestricted. (b) Characteristic of restricted rotation is a very shallow shoulder appearing about $q = 50$. This feature appears in curves C, D and G, but not in curves E and H, although a trace of it is evident in curve F. This shoulder is indefinite in the observed curve. (c) A shoulder appears near $q = 68$, very faintly on curve E and more prominently on H. These are "free-rotation" curves and H has a (S–S) bond of 2.23 Å. Since no trace of such a shoulder appears

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[13] I. L. Karle and J. Karle, *J. Chem. Phys.*, **17**, 1052 (1949); **18**, 957 (1950).

on the observed curve it appears that a model with completely free rotation probably has the (S–S) bond distance not greater than 2.20 Å., or that the predominance of the free-rotation contribution must be reduced. (d) The marked shoulder at $q = 57$ seems to be characteristic of free rotation and becomes more prominent with increasing (S–S) distance. The shoulder on the observed curve at this point may indicate a partially free rotation with an (S–S) distance not less than 2.20 Å. From an examination of the intensity curves it is clear that the main maxima and minima are fitted by models either with free or restricted rotation, and there are some minor features that support both free and completely restricted rotation.

A further comparison of the intensity curves of the models of Fig. 4 with respect to the positions of the maxima and minima is shown in Table VI.

TABLE VI

COMPARISON OF THE OBSERVED INTENSITY CURVE WITH COMPUTED CURVES

Model	$q_0$calcd./ $q_0$obsd.	Average deviation	r_{ij} for (S-S), Å.	$\left(\frac{q_0\text{calcd}}{q_0\text{obsd}}\right)(r_{ij})$
C	1.0134	0.017	2.16	2.189
D	1.0015	.016	2.20	2.203
E	1.0021	.016	2.20	2.205
F	0.9992	.018	2.20	2.198
G	1.0005	.015	2.23	2.231
H	0.9993	.016	2.23	2.228
			Average	2.209 ± 0.03 Å.

The value arrived at above, *i.e.*, (S–S) = 2.21 Å. is close to that obtained by the analysis of the radial distribution curve above, *i.e.*, 2.22 Å. The (S–F) bond length has been maintained at 1.56 Å. in these calculations on the basis of the single definite bell-shaped peak of the radial distribution curve. The final values for the distances are: (S–F) 1.56 ± 0.02 Å.; (S–S) 2.21 ± 0.03 Å. All bond angles are right angles.

Discussion of Results

The number of models with variations in structure that is compatible with the evidence of the electron diffraction pictures is strictly limited. A high degree of symmetry in any model is necessary in order to fit the spacings to the narrow peaks of the radial distribution curve because of the limited variation allowed. If one assigns a separation of 1.56 ± 0.01 Å. to the (S–F) bond, and a separation of 2.20 ± 0.02 Å. to the associated (F–F) bonds, the only model that accounts readily for the weights (nZ_iZ_j) assigned these spacings must contain an octahedral (SF_5) group with the FSF angles equal to 90°. The octahedral symmetry can be preserved by linking two such (SF_5) groups with a S–S bond in a sort of dumbbell structure, and this model is compatible with the electron diffraction pictures. Sulfur–sulfur links are well known, but normally the hexavalent sulfur atom is found in compounds containing only one sulfur. Trost and McIntosh[14] have decomposed the S_2F_{10} molecule thermally and suggested that the first point of rupture is the S–S link

$$S_2F_{10} \longrightarrow SF_5 + SF_5$$

which lends kinetic support to the structure proposed above. The chemical stability of the compound is due in part to the strength of the (S–F) bond (of the order of 88 kcal./mole[15]); further the (S–S) bond has considerable strength, with an estimated bond energy of 64 kcal./mole,[14] although it must be emphasized that this figure is given for a (S–S) bond of "normal" length (2.05–2.08 Å.), whereas a "stretched" bond (2.21 Å.), as is found in S_2F_{10}, may have a bond energy appreciably different from this figure.

According to Schomaker and Stevenson[16] the length of a bond can be estimated by adding the contributions from the atoms involved and making a correction (based on the net difference in electronegativity) for ionic character in the bond. Their formula, $r_{AB} = r_A + r_B - 0.09\,|r_A - r_B|$, when applied to the (S–F) bond gives $r_{AB} = 0.72 + 1.04 - 0.09\ (1.5) = 1.62_5$ Å. This bond length is about 0.07 Å. longer than the observed value for S–F but bond lengths shorter than that calculated by the above formula are found with many compounds of fluorine with the non-metals. A discussion of the subject has been given by Bauer.[17] The (S–F) bonds of SF_6 are suggested to be hybridized bonds of mixed ionic and covalent character,[14,18,19] sulfur having a double positive charge. The S–S bond is longer than would be postulated on a basis of the sum of covalent bond lengths, *i.e.*, 2.21 Å. found, 2.08 Å. calculated. Palmer[20] reports the (S–S) link in S_2Cl_2 to be 2.05 Å., in reasonable accord with the covalent sum, and Skinner[21] gives the value 2.07 Å., with the energy of the (S–S) link 52.9 kcal./mole. A reduction of the bond length to 2.08 Å. would reduce the separation of the peripheral fluorine atoms to 2.4 Å. in the interlocked position, a value considerably smaller than the suggested van der Waals radius.[22] If all the bond angles are to be 90°, stretching of the (S–S) bond is required to allow space for the fluorine atoms, and hindered rotation of one (SF_5) group relative to another is expected. The degree of the limitation of the rotation depends, of course, on the temperature and the mutual repulsion of the fluorine atoms. The root-mean-square vibrational displacement of the fluorine atoms of 0.07 Å. suggested by the radial distribution curves would allow a certain degree of rotational freedom. In this study the radial distribution and intensity curves suggest that restricted and free modes of rotation make roughly equal contributions to the diffraction effects.

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