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be only one linear combination of the functions based on the various frameworks which will have the correct symmetry.

CONCLUSION

It is to be emphasized that only symmetry considerations have been used in this paper so that the results are necessarily incomplete since they do not yield any information regarding the magnitudes of the splittings to be expected. Actual energy levels may not be split to an observable extent or they may show the splitting indicated here only incompletely. It is possible also that certain of the perturbations, especially

the rotation-vibration coupling, may split the approximate energy levels to such an extent that a component of one approximate level may nearly coincide with a component of another approximate level. In spite of these complications, however, the symmetry does restrict the maximum number of components which are possible and gives the selection rules and statistical weights involved. Experimental results[4] exist which may be capable of interpretation in terms of these effects but further work is necessary.

[4] W. B. Steward and H. H. Nielsen, Phys. Rev. **47**, 828 (1935).

The Molecular Structures of Sulfur Dioxide, Carbon Disulfide, and Carbonyl Sulfide

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The structures of the molecules SO₂, CS₂, and COS have been investigated by the electron diffraction method with the following results; SO₂, $S-O = 1.46 \pm 0.02A$; CS₂, $C-S = 1.54 \pm 0.03A$; COS, $C-O = 1.16 \pm 0.02A$, $C-S = 1.56 \pm 0.03A$. The types of bond arrangement compatible with these interatomic distances are discussed. In SO₂ the molecule resonates between the structures having single-double and double-single bonds between the sulfur and the two oxygen atoms, with a bond angle of $122° \pm 5°$. CS₂ is a linear molecule with the structure having the two double bonds predominating over those having a single and a triple bond. In COS the double-double bond arrangement and the structure having the triple carbon-oxygen bond predominate.

T HE molecular structures of sulfur dioxide, carbon disulfide, and carbonyl sulfide have been studied by the method of electron diffraction of gases. A jet of vapor is made to intersect a beam of forty-kilovolt electrons whose diffraction pattern is registered on x-ray film. Visual measurements on the maxima and minima are correlated with those on the theoretical curves based on various molecular models. In these curves the scattering power of an atom for electrons is assumed to be constant with angle and the inelastic scattering is neglected. A detailed discussion of the procedure used in interpreting electron diffraction photographs has already been published.[1]

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[1] L. Pauling and L. O. Brockway, J. Chem. Phys. **2**, 867 (1934).

SULFUR DIOXIDE

The sample of sulfur dioxide was redistilled from the purest commercial product.

The heavier photographs showed four maxima. The first was very strong; the second, strong and rather broad; the third and fourth were weaker but very sharp. The theoretical intensity curve, Fig. 1, is based upon a triangular model with an angle of 120° between the sulfur-oxygen bonds. No other curves are shown since the theoretical diffraction pattern is very insensitive to changes in bond angle. This effect in molecules with heavy central atoms and light outer atoms has been discussed for chlorine dioxide.[2]

The values obtained for the sulfur-oxygen distance are given in Table I. The third column

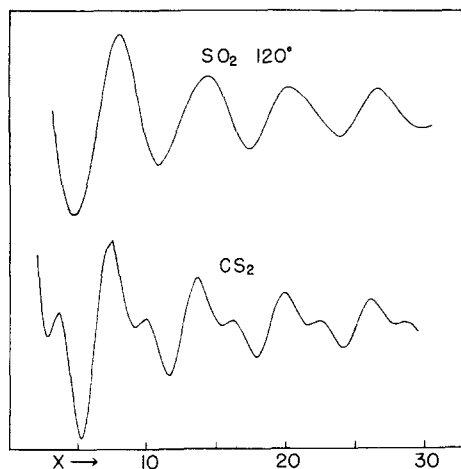[2] L. O. Brockway, Proc. Nat. Acad. Sci. **19**, 303, 874 (1933).

FIG. 1. Theoretical intensity curves for sulfur dioxide and carbon disulfide.

TABLE I. *Sulfur dioxide.*

FOUR PHOTOGRAPHS			$\lambda = 0.0606A$	
Max.	Min.	$\dfrac{4\pi \sin \theta/2}{\lambda}$	x	a
1		5.625	7.86	(1.396)
2		9.656	14.30	1.481
	3	11.99	17.27	1.441
3		13.76	20.15	1.464
	4	16.19	23.75	1.467
4		18.15	26.60	1.466
			Average	1.464
		$S-O = 1.46 \pm 0.02A$		

shows the observed positions of the maxima and minima, where θ is the scattering angle and λ is the wave-length associated with the electrons. The fourth column gives the positions of the maxima and minima on the theoretical curve and in the last column are listed the values of the sulfur-oxygen distance. The final value is $S-O = 1.46 \pm 0.02A$.

An earlier electron diffraction investigation of sulfur dioxide[3] leads to the value 1.37A. This was obtained with the aid of photographs showing only one maximum and is accordingly less reliable than the present result based upon measurements of four maxima and two minima.

The bond angle in SO_2 has been evaluated from the studies of the vibrational spectrum in the infrared region and by the Raman technique.[4] With the aid of the fundamental frequencies ($\nu_a = 1361$, $\nu_\pi = 1152$, $\nu_\delta = 525$ cm^{-1})[5] corresponding to the three modes of vibration, the treatment of the molecule, with the two-constant "valence

force" potential function and the assumption that the vibration is harmonic, leads to a value of $122° \pm 5°$. If this angle and the vibrational frequencies are used in conjunction with the Badger relation between the force constant and interatomic distance,[6] the sulfur-oxygen separation is calculated to be 1.48A, in satisfactory agreement with our results.

The electronic structures which seem likely to contribute to the ground state of sulfur dioxide are as follows:

I   II   III
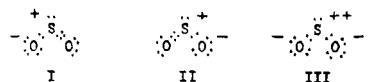
A structure can be written having single bonds and only three electron pairs on one of the oxygen atoms; but this is less likely than the third of the structures above because of the greater electron affinity of oxygen. In view of the theoretical possibility of placing five electron pairs on the sulfur atom, structures may be considered having two double bonds or a single and a triple bond, but these undoubtedly make very small contributions.

The observed bond distance is 0.05A less than the sum of the covalent radii[7] for double bonds. The double bond distance required by resonance between I and II above would be shortened by the polar character of the bonds. The inclusion of III in the resonating structures would not affect the distances but this structure is probably involved because of the tendency of sulfur to assume the double plus charge as in the sulfates and thionates.

[3] R. Wierl, Ann. d. Physik 8, 544 (1931).
[4] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. A137, 605 (1933); A138, 531 (1932). See also A. Jonescu, Comptes rendus 196, 1476 (1933); 197, 35 (1933); and J. H. Clements, Phys. Rev. 47, 224 (1935). We have not considered Jonescu's structure because of the incomplete nature of the rotational analysis upon which it is based, and the dependence upon Wierl's erroneous value of the $S-O$ distance.
[5] R. M. Badger and L. G. Bonner, Phys. Rev. 43, 305 (1933).

[6] R. M. Badger, J. Chem. Phys. 2, 128 (1934).
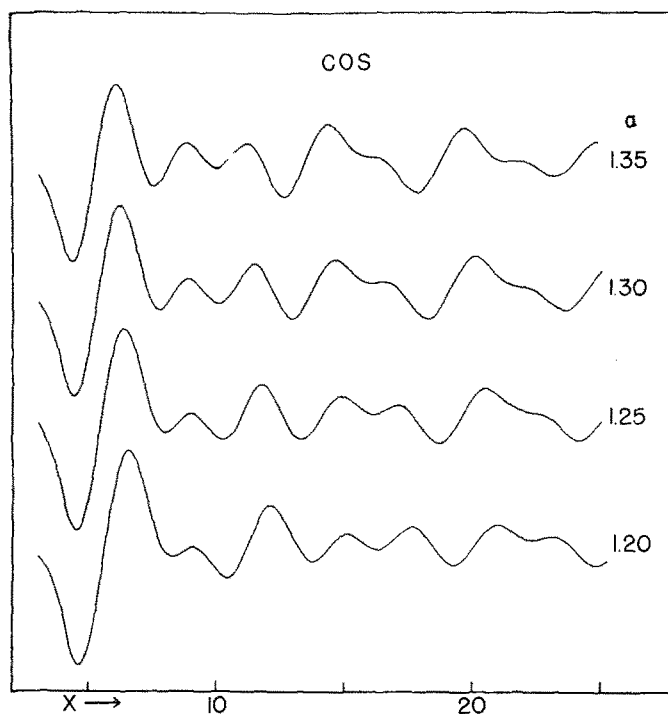[7] L. Pauling, Proc. Nat. Acad. Sci. 18, 293 (1932).

FIG. 2. Theoretical intensity curves for carbonyl sulfide.

The angle is determined by the separate electronic structures and the value determined spectroscopically is just that to be expected between a single and a double bond on a tetrahedral atom.

TABLE II. *Carbon disulfide.*

EIGHT PHOTOGRAPHS		$\frac{4\pi \sin \theta/2}{\lambda}$	$\lambda = 0.0607A$	
Max.	Min.		x	a
1		4.713	7.25	1.538
1a		6.312	9.85	1.560
	2	7.623	11.52	1.512
2		8.698	13.55	1.559
2a		10.63	16.10	1.515
	3	11.63	17.84	1.535
3		12.65	19.84	1,568
3a		14.58	22.40	1.536
	4	15.54	24.12	1.553
4		16.81	26.12	1.554
				Average 1.543

$$C - S = 1.54 \pm 0.03A$$

CARBON DISULFIDE

The carbon disulfide photographs were characterized by four strong maxima each followed by a weak maximum and a deep minimum. This appearance, which is also observed in the theoretical curve corresponding to a linear model (Fig. 1), is due to the fact that one of the two different interatomic distances in the molecule is just twice the other. The results given in Table II lead to a carbon-sulfur distance of $1.54 \pm 0.03A$ in essential agreement with Wierl's value[3] of 1.58A.

The electronic structures to be considered are the three having the double-double, the single-triple and the triple-single arrangement of bonds. If the three were of nearly equal importance the triple bond distance should be observed as in the analogous case of carbon dioxide. The table of radii gives 1.63A for the double bond and 1.43A for the triple bond. Observations on the

TABLE III. *Carbonyl sulfide.*

FIVE PHOTOGRAPHS			$\lambda = 0.0602A$			
Max.	Min.	$\dfrac{4\pi \sin \theta/2}{\lambda}$	$x_{1.35}$	$x_{1.30}$	$a_{1.35}$	$a_{1.30}$
1		5.23	6.05	6.18	1.156	1.181
	2	6.41	7.51	7.75	1.171	1.209
2		7.67	8.80	8.90	1.147	1.160
	3	8.70	9.95	10.10	1.144	1.161
3		9.82	11.15	11.45	1.135	1.165
	4	10.93	12.60	12.90	1.153	1.180
4		12.20	14.30	14.60	1.172	1.196
	5	13.33		15.90		1.193
5		14.04	16.15	16.60	1.151	1.182
	6	15.31	17.80	18.20	1.162	1.189
6		16.65	19.60	20.10	1.177	1.206
				Average	1.157	1.184
				(Ave. Dev.	0.011	0.013)

$$C-O = 1.16 \pm 0.02A$$
$$C-S = 1.56 \pm 0.03A$$

spectroscopic molecules P_2 and PN[8] indicate that the ratio of triple to single bond radius for elements in the second row of the periodic table should be larger than the value 0.79 used in the radius table. From $r_0 = 1.86A$ in $P \equiv P$ the triple bond radius for phosphorus is 0.93A. Adding to this the triple bond radius for nitrogen (0.55A) we get 1.48A in agreement with the observed value for $P \equiv N$ of 1.49A. Accordingly with the value 0.93A for the triple bond radius of phosphorus the triple-single bond radius ratio becomes 0.846 for second row elements. Applying this ratio to sulfur and adding the triple bond radius of carbon we obtain 1.49A for the predicted value of the carbon-sulfur triple bond.

The observed value 1.54A is 0.05A larger than the triple bond distance; therefore the contribution of the second and third structures above is considerably less important than that of the first. This conclusion is supported by the very

[8] G. Herzberg, Ann. d. Physik **15**, 677 (1932); J. Curry, L. Herzberg and G. Herzberg, Zeits. f. Physik **86**, 348 (1933).

small tendency of second row elements to form triple bonds; in fact, the two compounds of phosphorus mentioned in the preceding paragraph are the only known examples, and they exist only in an electrical discharge.

CARBONYL SULFIDE

Theoretical curves were calculated for four linear models of carbonyl sulfide corresponding to different ratios (a values in Fig. 2) of the carbon-sulfur to carbon-oxygen distances. That the second ring was observed to be very nearly as strong as the third and the maximum beyond the fourth was scarcely more than a shelf fixes the ratio of the two distances at about 1.34. Table III includes the calculations for the two models with ratios of 1.35 and 1.30. The final values are $C-O = 1.16 \pm 0.02A$ and $C-S = 1.56 \pm 0.03A$.

Dornte[9] obtained electron diffraction photographs of carbonyl sulfide and reported calculations of the theoretical scattering for only one model (corresponding to a distance ratio of 1.40). This ratio and the distance which he reports ($C-O = 1.13 \pm 0.05A$, $C-S = 1.58 \pm 0.08A$) differ from ours by less than the uncertainty which he ascribes to his measurements.

The value observed for the carbon-sulfur separation is essentially the same as that in the CS_2 molecule while the carbon-oxygen distance agrees with the value 1.15A in carbon dioxide and with the triple bond radius sum 1.13A. The foregoing discussion of the character of the carbon-sulfur bond applies also to the case of carbonyl sulfide.

We are grateful to Professor Linus Pauling for suggestions and criticisms.

[9] R. Dornte, J. Am. Chem. Soc. **55**, 4126 (1933).