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The Nuclear Separation of the S_2 Molecule by Electron Diffraction

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Rotational analyses of S_2 bands as carried out by various workers have led to the following values for the nuclear separation; 1.60A, 1.84A, 1.73A, and 1.93A. In the present work this distance was determined by electron diffraction from S_2 vapor at 800°C and was found to be 1.92 ± 0.03A. This value is based upon the measured relative intensities of scattering in the region of the third maximum, $(1/\lambda) \sin \frac{1}{2}\theta$ from 0.70 to 1.0, and upon visual measurements on the fourth, fifth and sixth diffraction maxima. When the temperature of sulphur vapor is decreased appreciably below 800°C its electron diffraction pattern shows the presence of higher molecular types. The results obtained can be explained on the basis of S_{2+n} molecules where $n = 1, 2, 3 \cdots$ with a S—S—S valence angle of about 100° and a S—S distance, between closest neighbors, of *ca.* 2.1A. These values are in agreement with those found for the symmetrical puckered ring-shaped S_8 molecule present in crystalline sulphur.

INTRODUCTION

CONSIDERABLE uncertainty has existed concerning the correct rotational analysis of the diatomic sulphur bands. This is caused by the complexity of the spectrum for there is found considerable overlapping of the lines which has made the analysis difficult. As a result, the internuclear separation obtained from the band spectra measurements has been in dispute. Electron diffraction from gases gives directly the internuclear separation free from the difficulties inherent in band spectra analysis. It has been tested for its accuracy by comparison with band spectra data for the diatomic molecules Cl_2,[1] Br_2[2] and I_2.[3] In these cases complete agreement has been obtained, therefore we expect that equally good agreement must be found in the case of S_2.

The situation concerning the nuclear separation of the S_2 molecule is summarized below. (1) Naudé and Christy[4] studied five ultraviolet emission bands of S_2 taken in the third order of a 21-ft./grating (0.87A/mm). A study of the rotational structure of these bands showed that they were due to the same type of electronic transitions as found for the Schumann Runge bands of O_2, i.e., ${}^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-$. The nuclear separation of the lower state r_e'' was found to be $\mathbf{1.60 \times 10^{-8}}$ **cm.** Also since alternate levels were missing it was concluded that the angular momentum of the S^{32} nucleus is zero. Independently P. Swings[5] reported to have confirmed the results of Naudé and Christy from an investigation of the fluorescence spectra of S_2. (2) Badger[6] pointed out that the value of 1.60A for the internuclear distance of S_2 seemed very abnormal according to expected covalent bond radii and to certain empirical rules by which the internuclear distances can be calculated from vibrational frequencies. He found that the measured lines obtained by Naudé and Christy could be reassigned to the various branches so that a different set of combinations could be obtained. This revised treatment led to $\mathbf{r}_e'' = \mathbf{1.84A}$. Badger however concluded that the sulphur molecule is antisymmetrical in the nuclei. (3) Van Dijk and Lameris[7] took new photographs in the 4th order of a 21-ft. grating (0.6A/mm) and reported that they failed to find on their plates a great many lines given by Naudé and Christy. On making a new analysis of the S_2 bands they obtained a value of **1.73A** for the internuclear distance. The wave functions of the S_2 molecule were found by them to be symmetrical in the nuclei. (4) In an abstract[8] of the present work it was shown that the nuclear separation of the S_2 molecule as found by electron diffraction was $\mathbf{1.94 \pm 0.03A}$, a value definitely greater than any of the previous band spectra measurements. (5) Recently Olsson[9] carried out

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[1] L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. **19**, 68 (1933). See also, J. Am. Chem. Soc. **57**, 2684 (1935).

[2] R. Wierl, Ann. d. Physik **8**, 521 (1931).

[3] S. B. Hendricks, L. R. Maxwell, V. M. Mosley and M. E. Jefferson, J. Chem. Phys. **1**, 549 (1933).

[4] S. M. Naudé and A. Christy, Phys. Rev. **37**, 490 (1931).

[5] Reference 4, note added in proof.

[6] R. M. Badger, Phys. Rev. **46**, 1025 (1934).

[7] E. W. Van Dijk and A. J. Lameris, Physica **2**, 785 (1935).

[8] Baltimore Meeting November 30, 1935, Phys. Rev. **49**, 199 (1936).

[9] E. Olsson, Zeits. f. Physik **99**, 114 (1936).

a rotational analysis of S_2 using Naudé and Christy's data for seven bands in the ultraviolet. He finds zero nuclear spin and a nuclear separation in the ground state of **1.93A.**

PROCEDURE

The intensity of electron scattering $I(x)$ from diatomic sulphur can be expressed as follows:

$$I(x)=k\left\{2\psi_s^2(1+\sin x/x)+\frac{32\cdot S(\nu_s)}{(\sin\frac{1}{2}\theta/\lambda)^4}\right\},\quad (1)$$

where $$x=4\pi l_{s-s}(1/\lambda)\sin\tfrac{1}{2}\theta.\quad (2)$$

l_{s-s} is the separation of the sulphur atoms while the remaining terms are expressed in the usual notation.[10] Intensity distribution calculated from this equation is shown in Fig. 1. It is noticed that the interference properties appear only as slight humps on a smooth curve; however for sake of convenience they will be referred to as maxima. After first drawing a continuation of the smooth portion of the curve through the region of variation then the position of these maxima are determined by a vertical line which approximately divides the enclosed area into equal parts. An arbitrary method of this kind is entirely justifiable provided exactly the same procedure is used for locating the maxima on the corresponding experimental scattering curve. After having determined the position of the theoretical maxima in terms of x and the experimental maxima in terms of $(1/\lambda)\sin\frac{1}{2}\theta$, l_{s-s} is immediately obtained from Eq. (2).

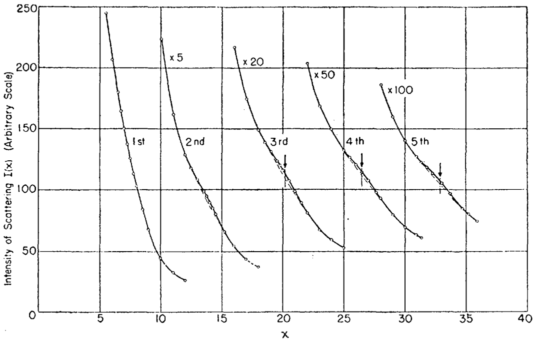

FIG. 1. Theoretical electron scattering curve for S_2.

EXPERIMENTAL ARRANGEMENT

In order to obtain a source of S_2 molecules free from association it was necessary at the pressures used (*ca.* 60 mm Hg) to raise the temperature of the gas to about 800°C. Under these conditions dissociation of sulphur vapor into S_2 is almost complete.[11]

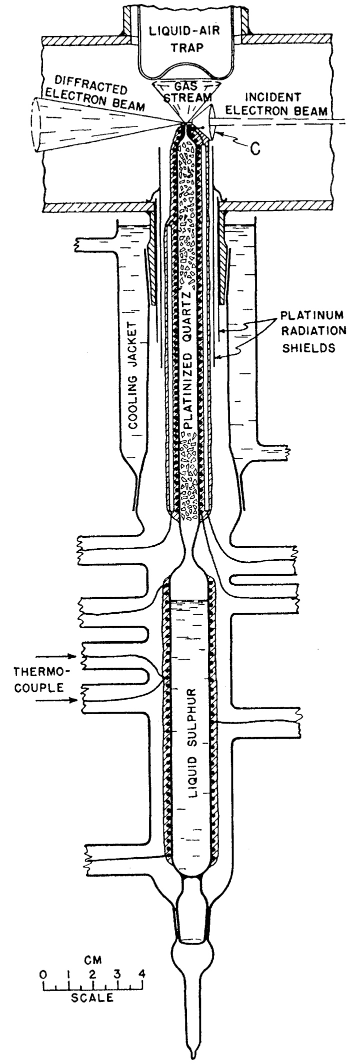

FIG. 2. Diagram showing sulphur boiler and heating tube for producing S_2 vapor. Gas jet and electron diaphragm are mounted together.

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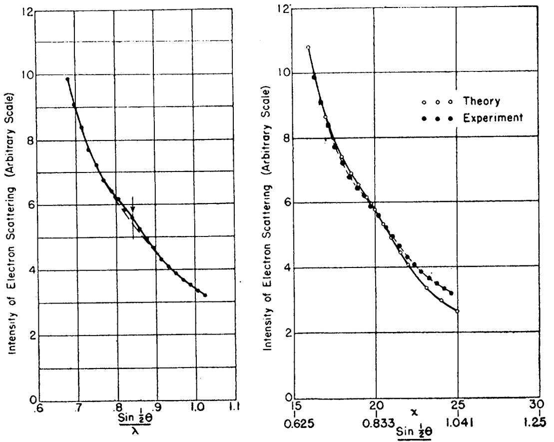
[10] R. Wierl, Ann. d. Physik **8**, 521 (1931). For a formulation of the incoherent scattering, see for instance L. Bewilogua, Physik. Zeits. **33**, 688 (1932). The F values used were obtained from the calculated values of R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931), and also from L. Pauling and J. Sherman, Zeits. f. Krist. **81**, 1 (1932).

[11] G. Preuner and W. Schupp, Zeits. f. physik. Chemie **68**, 129 (1909).

Electron diffraction photographs were taken from S_2 vapor produced from two different sources: first, from iron pyrite (FeS_2) at 850°C which readily decomposes into FeS and S_2 giving an ample source of S_2;[12] second, by passing sulphur vapor through a bed of hot platinized fused quartz pieces at 800°C as illustrated in Fig. 2. The inner tube containing the sulphur and the platinized quartz was made of fused quartz and was wound with platinum wire for heating. The platinum cone *C* containing a hole 0.11 mm in diameter defined the size and location of the electron beam while the gas jet in proper position had a diameter of 0.25 mm and length of 3 mm. The important features of this type of assembly have been previously discussed.[13] Temperature measurements of the heater tube and gas jet were made by the use of an optical pyrometer. The electron diffraction pattern was recorded on a photographic plate (insensitive in the red) at a distance of 10.0 cm using generally a de Broglie wave-length of 0.060A. Final relative intensity scattering curves were obtained by transforming the densitometer records obtained into intensity curves by the use of calibration plates made from electron exposures.

RESULTS AND DISCUSSION

Electron diffraction photographs obtained showed no diffraction rings at the smaller values of $(1/\lambda)\sin\frac{1}{2}\theta$. This is to be expected from the theoretical scattering curves, for it is seen in Fig. 1 that the first maximum is entirely absent while the second is barely detectable thus giving no ring suitable for measurement until the third maximum is reached. A typical experimental intensity of scattering curve obtained in the region of the third maximum is shown in Fig. 3a. This prominence appears very similar in shape to the corresponding theoretical maximum and from its position a S−S distance of 1.91±0.02A is obtained. Direct comparison between observed and calculated intensities is shown in Fig. 3b. In general good agreement between the two curves is obtained; however the experimental intensity curve is found to decrease slightly less rapidly than does the theoretical curve.



(a) (b)

FIG. 3a. Experimental electron scattering curve for S_2. 3b. Comparison between theoretical and experimental electron scattering curves of S_2 for a S−S distance of 1.91A. The two curves were made to fit in intensity at $x=20.2$.

Position of the fourth, fifth and sixth maxima were measured visually. The positions of these maxima are not only useful in determining l_{s-s} but also confirm the fact that the vapor used was diatomic, i.e., l_{s-s} was found to be independent of the maximum used. *Visual measurements were also made on electron diffraction photographs obtained from Cl_2 vapor* for purposes of comparison, since Cl_2 and S_2 give almost the same type of diffraction pattern. Visual measurements on the 4th, 5th and 6th maxima of Cl_2 gave $l_{Cl-Cl}=2.00+0.02$A in agreement with the band spectra value of 1.98A. For the case of the visual measurements on the 5th and 6th maxima the values of x used in Eq. (2) were simply the maxima of the $\sin x/x$ function. These values of $x_{\max}$ do not differ appreciably from those found by using the exact formula in the manner described above. One should expect therefore that the visual measurements on S_2 should agree with the band spectra value to within about one percent.

Final results of the visual measurements, together with a summary of all the data obtained, are given in Table I. Good agreement between the visual and intensity determination is found. The position of the third maximum for S_2 from FeS_2 was located from the densitometer records in a manner similar to that used on the intensity curves. By considering all the data

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[12] For data on the dissociation pressure of pyrite, see E. I. Allen and R. H. Lombard, Am. J. Sci. **43**, 175 (1917).

[13] L. R. Maxwell, S. B. Hendricks and V. M. Mosley, J. Chem. Phys. **3**, 699 (1935).

TABLE I. *Summary of electron diffraction photographs of S_2.*

	1st Max.	2nd Max.	3rd Max.	4th Max.	5th Max.	6th Max.
S_2 vapor from FeS_2:						
Exp. values for $(1/\lambda)\sin\frac{1}{2}\theta$	—	diffuse halo	0.827 ± 0.008	1.09 ± 0.02		
Method of measurement	—	—	from dens. rec.	visual		
$x_{\max}$ theoretical curve	none	very slight	20.2	26.5		
l_{s-s}	—	—	1.94 ±0.02A	1.93±0.03A		
S_2 vapor from sulphur passed through platinized quartz pieces at 850°C						
Exp. values for $(1/\lambda)\sin\frac{1}{2}\theta$	—	diffuse halo	0.840 ± 0.004	1.10 ± 0.005	1.37	1.63
Method of measurement			from exp. int. curve	visual	visual	visual
$x_{\max}$ theoretical curve	none	very slight	20.20	26.5	32.95	39.24
l_{s-s}	—	—	1.91 ±0.02	1.92±0.01	1.91±0.01	1.92±0.02

Most probable separation of S_2 molecule in normal state is 1.92±0.03A.

obtained we arrive at **1.92±0.03A as the average value for the S−S nuclear separation of S_2.** The distance 1.93A given by Olsson from band spectra analysis is in close agreement with the final electron diffraction value which indicates that only his rotational analysis of S_2 can possibly be correct.

TEMPERATURE EFFECT AND THE HIGHER MOLECULAR FORMS OF SULPHUR

Intensity corrections for S_2

Since high gas temperatures were necessary for electron diffraction from S_2 some consideration must be given concerning the mutual molecular vibrations present and how they will affect the intensity of scattering. James[14] has shown for x-ray scattering from gaseous diatomic molecules that the temperature correction appears in the form of e^{-A} which is a variable coefficient of the term $\sin x/x$ in Eq. (1). A is defined by the relation

$$A=\frac{h}{\mu\nu}\coth\frac{h\nu}{2kT}\cdot\left(\frac{\sin(\theta/2)}{\lambda}\right)^2,$$

where μ is the reduced mass, T the absolute temperature, k the Boltzmann constant and ν the frequency of the oscillator. This correction can be used directly for the case of electron scattering and it was found for S_2 to make only a very slight change in the intensity of scattering. Also one can see directly that the temperature could not produce any appreciable errors in the determination of the nuclear separation because at these temperatures (1073°K) about 60 percent of the molecules are still in the ground state with less than 25 percent in the first vibrational level and about 9 percent in the second vibrational level. The mean time position of the molecule estimated from this population of the different vibrational levels is to within less than ½ percent of the equilibrium position in the ground state.

ELECTRON DIFFRACTION FROM THE HIGHER MOLECULAR FORMS OF SULPHUR

When the temperature of the sulphur gas is appreciably decreased below 800°C the electron diffraction pattern changes completely. A prominent ring comes at $(1/\lambda)\sin\frac{1}{2}\theta=0.516\pm0.005$ (measured from densitiometer records) and an outer ring at 0.790 ± 0.008 which was measured both visually and from the densitometer traces. These results clearly indicated the formation of S_{2+n} molecules in the gas where $n=1, 2, \cdots$. The structure was determined approximately and it was found that the molecule must have a S−S−S valence angle of about 100° and approximately 2.1A as the S−S distance between neighboring atoms. Below 96°C sulphur crystallizes into a stable orthorhombic form. Warren and Burwell[15] have shown from x-ray diffraction data that this structure contains S_8 molecules in the shape of symmetrical puckered rings. They arrived at a S−S distance of 2.12A between

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[14] R. W. James, Physik. Zeits. **33**, 737 (1932).

[15] B. E. Warren and J. T. Burwell, J. Chem. Phys. **3**, 6 (1935).

closest neighbors and a bond angle of 105°, values with which the electron diffraction results are in close agreement. Apparently the valence angle and the nuclear separations are maintained even when molecules are formed in a gas at high temperature where the S_8 ring is probably broken, leaving molecular chains of irregular lengths.

The writers wish to thank Dr. O. R. Wulf and Dr. E. J. Jones for the interest they have shown in this work.

Note added in proof: June 3rd, 1936. From a more recent rotational analysis of S_2, Olsson[16] has found $r_e''=1.88$A which is somewhat lower than his previous value of 1.93A; both values are only slightly different from the final electron diffraction value 1.92 ± 0.03A. He further suggests that the electron diffraction results should be slightly higher than the band spectra value because of the presence of molecular vibrations. The importance of considering the molecular vibrations in electron diffraction measurements has been discussed above. It can be seen that no appreciable differences in the internuclear distances in S_2 can be attributed to a temperature effect.

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[16] Olsson, Nature **137**, 745 (1936).

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Radio and the Sunspot Cycle

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The observed optimum frequency f for long distance daylight communication averaged over the year during the period from 1923 to 1936 was found to vary with the yearly average relative sunspot number s according to the relation $f=7.8(s+12)^{\frac{1}{2}}$. The march of the sunspot curve from 1749 to 1935 suggests the possibility of greater sunspot numbers in coming solar cycles than the value $s=78$ which occurred at the 1928 maximum. By means of the f,s relation, radio conditions for sunspot numbers from 100 to 160 are calculated.

It is well known that radio communication phenomena vary with the cycle of solar activity. In the following paragraphs, radio and solar data are assembled to bring out the relations which exist. The radiofrequencies useful for long distance daylight communication during the years 1923 to 1936 are found to fall in more closely with the yearly average sunspot numbers than with the magnetic character and solar constant during this period.

In Fig. 1 are plotted the values of the optimum frequencies for daylight communication for 1000, 3000 and 5000 nautical miles averaged over the year for the years from 1923 to 1936. The period covers the cycle of solar activity with minima in 1923 and 1933 and the maximum in 1928. In the first two columns of Table I are given further radio observations for the years 1928 and 1933. The data were assembled from published radio literature[1] and refer to world-wide conditions. Experience has shown that the optimum frequency is that frequency which places the receiver in the zone of reception beyond the fewest number of areas of skip.

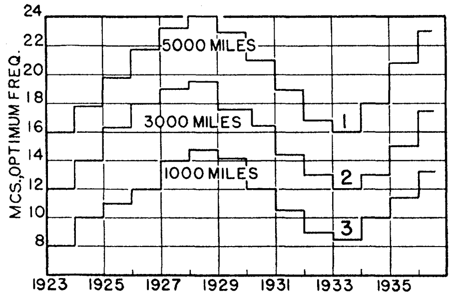

FIG. 1. Optimum frequencies for daylight communication.

TABLE I. *Observed and calculated relationship between sunspot number and optimum radiofrequency for long distance day communication.*

	Observed					
Year	1928	1933	Calculated from (2)			
Sunspot number	78	5.7	100	120	140	160
Long distance day communication						
Optimum	24 megacycles	16	25.3	26.4	27.4	28.4
Many cases	30–33	20–22	32–35	33–36	34–38	35–39
Occasional	33–36	22–24	35–38	36–40	38–41	39–43
Few	above 38	25	40	41	43	45

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[1] Particular mention may be made of the Technical Publications, Bell Telephone System; of papers by Prescott, Proc. Inst. Rad. Eng. **18**, 1797 (1930); and by Mögel, Telefunken Zeitung, Nr. 67, 23 (1934).