

## Microwave Spectrum and Molecular Structure of Disulphur Dichloride, S<sub>2</sub>Cl<sub>2</sub>

By COLIN J. MARSDEN, RONALD D. BROWN,\* and PETER D. GODFREY

(Department of Chemistry, Monash University, Wellington Road, Clayton, Victoria, 3168, Australia)

*Summary* The microwave spectrum of S<sub>2</sub>Cl<sub>2</sub> has been observed and analysed, leading to precise geometrical parameters and <sup>35</sup>Cl quadrupole coupling constants; the

SS bond length is shorter than the standard single bond length but not as short as that in S<sub>2</sub>F<sub>2</sub>.

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DISULPHUR DIFLUORIDE  $S_2F_2$  is the only disulphide known to exist in two stable isomeric forms, the 'unexpected' isomer,  $S=SF_2$ , being more stable thermodynamically than the symmetrical isomer FSSF. Moreover the symmetric FSSF has an unexpectedly short S-S distance, being very similar to that in the other isomer and also to the bond length in the  $S_2$  molecule.<sup>1,2</sup> Although the short S-S and long S-F bonds in  $S_2F_2$  have been rationalised in qualitative MO terms,<sup>1</sup> it is not clear that these structural features could have been predicted in advance. It is important to discover whether the unusual structural features of  $S_2F_2$  are unique or whether they show up in closely related compounds such as  $S_2Cl_2$ . It has recently been claimed that u.v. irradiation of  $S_2Cl_2$  in an argon matrix produces  $SSCl_2$ .<sup>3</sup> We report here the results of an initial microwave study of  $S_2Cl_2$  designed to yield precise geometrical data and evidence of the possibility of more than one isomer.

The microwave spectrum of  $S_2Cl_2$  was studied in a conventional Stark-modulated X-band cell, in the frequency range 8–40 GHz. The  $S_2Cl_2$  was continuously pumped through the cell, which for most measurements was cooled to ca.  $-60^\circ C$ , at pressures of 0.5–3 Pa. A commercial sample of  $S_2Cl_2$  was used, no impurities being detected in it by mass spectroscopy.

$S_2Cl_2$  is a prolate asymmetric rotor whose dipole moment is aligned along the  $b$  inertial axis. Its dense microwave spectrum is dominated by long series of  $Q$ -branches. The relatively weak low- $J$   $R$ -branch transitions were assigned by recognising their characteristic Stark modulation behaviour and quadrupole hyperfine patterns. Individual multiplets were analysed interactively using procedures outlined elsewhere;<sup>4</sup> the quadrupole coupling constants for  $^{32}S_2^{35}Cl_2$  were found to be  $X_{aa} = -7.35(10)$  MHz,  $X_{bb} = -16.05(5)$  MHz (quantities in parentheses are standard deviations in units of the last significant figure). Observed frequencies of a selection of rotational transitions for the two isotopic species are listed in Table 1 together with the

TABLE 1. Some of the observed rotational transition frequencies for the two main isotopic species of  $S_2Cl_2$ , and the derived rotational constants in MHz.<sup>a</sup>

	$^{32}S_2^{35}Cl_2$	$^{32}S_2^{35}Cl^{37}Cl$
$5_{33} \leftarrow 4_{22}$	34196.435	33757.32
$6_{34} \leftarrow 5_{23}$	36765.25	36269.68
$10_{19} \leftarrow 9_{28}$	17628.438	17017.51
$12_{12} \leftarrow 11_{011}$	31401.283	30749.55
$10_{28} \leftarrow 10_{19}$	10575.915	10505.557
$20_{317} \leftarrow 20_{218}$	16168.479	16023.41
A	5533.19(16)	5475.441(19)
B	1393.840(5)	1361.852(6)
C	1232.672(6)	1205.179(8)

<sup>a</sup> Frequencies listed are the centre of quadrupole multiplets; see text for discussion. Experimental uncertainties are thought to be  $< 15$  kHz for lines quoted to kHz precision, and  $< 30$  kHz otherwise. The rotational constants were derived by a least squares procedure which included quartic centrifugal distortion terms. The r.m.s. deviation between observed and calculated frequencies is 80 kHz for  $^{32}S_2^{35}Cl_2$  (33 transitions) and 84 kHz for  $^{32}S_2^{35}Cl^{37}Cl$  (27 transitions).

rotational constants derived from our spectral analysis. The microwave transitions that we have assigned for sulphur monochloride are consistent with a spectrum arising from the symmetric isomer of sulphur monochloride which has previously been shown by electron diffraction<sup>5</sup> and vibrational spectroscopy<sup>6</sup> to be the dominant isomer.

No evidence was obtained of the existence of lines that could be ascribed to a second isomer of this molecule.

Kraitchmann's equations<sup>7</sup> can be used to determine the location of the Cl atoms with respect to the centre of mass, from the difference in moments of inertia of the two isotopic species studied, and the S atoms can then be positioned from the observed values of the moment of inertia of one isotopic species. This method relies on the size of the difference between two quantities of comparable magnitude; although the original rotational constants were determined with high precision, the averaging effects caused by the zero point vibrational motion render some of the precision illusory. The S atoms can, in fact, be located in two different ways; either the  $b$  co-ordinate can be determined directly by the first moment condition, and the  $a$  and  $c$  co-ordinates from  $I_c$  and  $I_a$  (approach A), or the first moment condition can be neglected, and all three sulphur co-ordinates determined from the three simultaneous equations involving the three moments of inertia (approach B). The difference between the two sets of structural parameters is negligible in comparison with their probable deviation from equilibrium geometry data (typically several tenths of a picometre for bond lengths, a few tenths of a degree for angles). In Table 2 we present the atomic co-ordinates derived in the two ways and the resulting geometric parameters with their uncertainties due to random errors only.

TABLE 2. Atomic co-ordinates with respect to the centre of mass and geometrical parameters for  $^{32}S_2^{35}Cl_2$

	Approach A	Approach B
Cl	$a/\text{pm} \pm 206.816$	$\pm 206.816$
	$b/\text{pm} + 68.845$	$\pm 68.845$
	$c/\text{pm} \pm 19.229$	$\pm 19.229$
S	$a/\text{pm} + 80.503$	$\pm 80.540$
	$b/\text{pm} - 75.298$	$- 75.258$
	$c/\text{pm} \pm 54.988$	$\pm 55.042$
$r(S-S)^a/\text{pm}$	194.98	195.04(12) [193.1(5)]
$r(S-Cl)^a/\text{pm}$	205.52	205.52(7) [205.7(2)]
$\angle SScI^a/^\circ$	107.69	107.66(5) [108.2(0.3)]
$\angle$ (dihedral)		
$ClSSCl^a/^\circ$	85.19	85.24(10) [85.8(1.3)]

<sup>a</sup> Electron diffraction results (from ref. 5b) in brackets.

Several electron diffraction studies on  $S_2Cl_2$  have been performed. In Table 2 we compare the results of the most recent investigation<sup>5b</sup> with our work. An earlier study<sup>5a</sup> reported less precise values not significantly different from those given in ref. 5b. There is good agreement between the results of our work and the electron diffraction study apart from the value of the S-S bond length. The geometrical parameters derived from the electron diffraction studies have a simple physical meaning whereas those from our microwave data contain uncertainties related to zero-point vibrations. The electron diffraction parameters, however, are affected by correlation and are less precise than the microwave set. The present results definitely imply a longer S-S bond (by ca. 2 pm) than the electron diffraction value.

The S-S bond length in  $S_2Cl_2$  is ca. 10 pm shorter than 'typical S-S single bonds,' as found for example in  $S_8$ ,<sup>8</sup> and ca. 6 pm longer than in FSSF.<sup>1</sup> Such a result is in keeping

with the electronegativities of F and Cl. Given that Cl and  $\text{CF}_3$  are considered to have very similar electronegativities, the S-S bond length of 205(2) pm reported in a visual electron diffraction study of  $(\text{CF}_3\text{S})_2$ <sup>9</sup> seems anomalous.

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