Infrared and Raman Spectra of Cycloheptasulphur

By **Margaret Gardner** and **Astri Rogstad,*** Department of Chemistry, The University, Southampton

The i.r. and Raman spectra of cycloheptasulphur are reported. The fundamentals are assigned in terms of C_s symmetry and compared with those of S_8 and S_6. Force fields transferred from S_8 and S_6 provided fair agreement between calculated and experimental frequencies of S_7.

THE form of sulphur which is thermodynamically stable at room temperature, S_8, has been investigated[1-8] several times both by vibrational spectroscopy and by normal co-ordinate analysis. The results are consistent with the presence of puckered rings of D_{4d} symmetry in the solid, melt (below 193 °C), and solutions. Raman studies of saturated sulphur vapour at 180 and 250 °C show the presence of S_6 and S_8 in the gas phase[9] and also suggest the presence of S_7. Mass spectrometry[10] has shown that sulphur vapour contains all cyclo-species from S_2 to S_{10}. The early assignment of the vibrational spectra of S_8, by Bernstein and Powling,[2] has recently been revised after extensive normal co-ordinate calculations and investigations of the thermodynamic functions.[3-5]

A metastable modification of sulphur[11] (Engel's sulphur) was known as early as 1891. Raman and i.r. spectra[12,13] have been interpreted in terms of puckered S_6 rings of D_{3d} symmetry in both the solid state and in solution. A normal co-ordinate calculation[13] using the force field determined for S_8 has given a reasonable fit to the observed frequencies.

Recently Schmidt *et al.*[14,15] worked out the first procedures for kinetically controlled chemical synthesis of thermodynamically unstable sulphur rings. Molecules such as S_7, S_9, S_{10}, S_{12}, and S_{18} have been isolated and studied by mass spectrometry.[15-17] However, no studies of the vibrational spectra of these molecules have yet been reported.

In the course of our work[18] on identification of the

---

* *Present address:* Department of Chemistry, University of Oslo, Oslo 3, Norway.

[1] H. Gerding and R. Westrik, *Rec. Trav. chim.*, 1943, **62**, 68.

[2] H. J. Bernstein and J. Powling, *J. Chem. Phys.*, 1950, **18**, 1018.

[3] G. B. Guthrie, D. W. Scott, and G. Waddington, *J. Amer. Chem. Soc.*, 1954, **76**, 1488.

[4] D. W. Scott and J. P. McCullough, *J. Mol. Spectroscopy*, 1961, **6**, 372.

[5] D. W. Scott, J. P. McCullough, and F. H. Kruse, *J. Mol. Spectroscopy*, 1964, **13**, 313.

[6] G. M. Chantry, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, 1964, **20**, 1223.

[7] G. A. Ozin, *J. Chem. Soc.* (*A*), 1969, 116 and references cited therein.

[8] S. J. Cyvin, *Acta Chem. Scand.*, 1970, **24**, 3259 and references cited therein.

[9] I. R. Beattie, G. A. Ozin, and R. O. Perry, *J. Chem. Soc.* (*A*), 1970, 2071.

[10] J. Berkowitz, 'Elemental Sulphur,' ed. B. Meyer, Interscience, New York, 1965; see also J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, 1963, **39**, 275.

[11] M. Engel, *Compt. rend.*, 1891, **112**, 866.

[12] L. A. Nimon, V. D. Neff, R. E. Cantley, and R. O. Buttlar, *J. Mol. Spectroscopy*, 1967, **22**, 105.

[13] J. Berkowitz, W. A. Chupka, E. Bromels, and R. L. Belford, *J. Chem. Phys.*, 1967, **47**, 4320.

[14] M. Schmidt, B. Block, H. D. Block, M. Köpf, and E. Wilhelm, *Angew. Chem.*, 1968, **80**, 660.

[15] M. Schmidt and E. Wilhelm, *Chem. Comm.*, 1970, 1111.

[16] M. Schmidt and E. Wilhelm, *Angew. Chem.*, 1966, **78**, 1020.

[17] U.-I. Záhorszky, *Angew. Chem.*, 1968, **80**, 661.

[18] K. K. Yee, R. F. Barrow, and A. Rogstad, *J.C.S., Faraday II*, 1972, **68**, 1808.

various species in the gas-phase Raman spectrum of sulphur, we have recorded the Raman spectrum of cycloheptasulphur in the solid state and in solution, and the i.r. spectrum of the solid. The spectra are assigned and compared with cyclo-octasulphur and cyclohexasulphur. The force fields which have been used for these molecules are used to calculate frequencies for S_7.

RESULTS AND DISCUSSION

The i.r. and Raman spectra are shown in Figures 1 and 2 and the observed frequencies and assignment for S_7 are given in Table 1. The assignment is compared directly with those for S_6 and S_8.

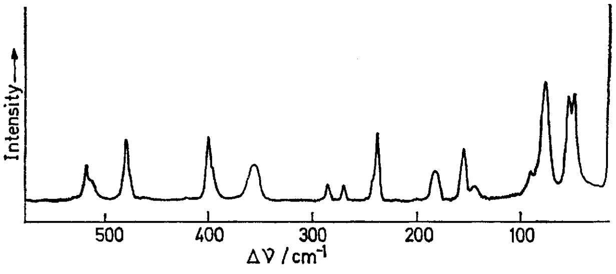

FIGURE 1 The Raman spectrum of solid cycloheptasulphur

The solution Raman spectrum was weak, and the state of polarisation could not be determined for all the bands.

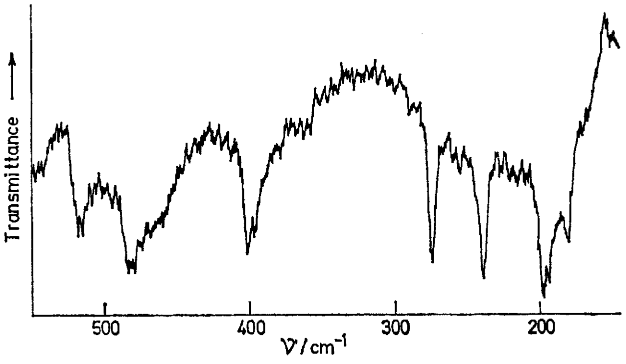

FIGURE 2 The i.r. spectrum of solid cycloheptasulphur

However, 5 bands are clearly polarised, including the 2 strongest bands in the spectrum at 236 and 483 cm^{-1}. It seems likely that these correspond to the 2 a_{1g} modes in S_6 at 266 and 471 cm^{-1}, and the 2 a_1 modes in S_8 at 218 and 475 cm^{-1}. The totally symmetric stretch shows little change in frequency with change in ring size, but the frequency of the totally symmetric deformation increases markedly with decreasing ring size from 218 cm^{-1} in S_8 through 236 cm^{-1} in S_7 to 266 cm^{-1} in S_6. The other non-degenerate deformation is an i.r.-active band at 313 cm^{-1} in S_6 (a_{2u}) and 243 cm^{-1} in S_8 (b_2). These probably correspond to the strong i.r. band at 274 cm^{-1} in S_7. This mode also shows a marked increase in frequency with decreasing ring size, comparable with that shown by the totally symmetric deformation. The lowest Raman-active fundamental, almost certainly associated with torsional motion of the molecule, shows an even more dramatic increase from 85 cm^{-1} in S_8 (e_2)

TABLE 1

I.r. and Raman spectra and assignment for S_7 and comparison with S_6 and S_8

S_6(ref. 13)			S_7				S_8 (ref. 4)		
I.r. solution	Raman solution	Assignment	I.r. solid	Raman		Assignment	I.r. solution	Raman solution	Assignment
				solid	solution				
				50vs		Lattice			
				54vs		Lattice			
				76vs		Lattice		86s,d	e_2
				90w,sh					
	204s	e_g	146m	145w,br		a'		152s,d	e_2
				155s	153s,d	a''			
180s		e_u	180m	184s		a'	191s	184w	e_1
			193m			a''			
			197m						
	266s,p	a_{1g}		238vs	236vs,p	a'		218s,p	a_1
			239vs	242sh		a''		248w	e_3
312s		a_{2u}	274vs	270w	268w	a'	243s		b_2
				285w	288w	a''			
			360sh	356s,br	362s,p	a'		437w,d	e_3
390vw		a_{1u}	396sh	397sh		a''	(411)		b_1
			402s	403vs	402m,p	a'			
	451w,d	e_g	476sh	477sh		a''		(475)	e_1
	476s,p	a_{1g}	482s	481vs	483s,p	a'		475s,p	a_1
62s		e_u	515m	516sh	510sh	a''	471s		e_2
			518m	519m	517m,p	a'			

s = Strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, p = polarised, d = depolarised.

The S_7 molecule is a puckered seven-membered ring and *X*-ray structural data for the *xy*-projection has been determined.[19] The only symmetry element the molecule can possess is a mirror plane. Assuming C_s symmetry, the 15 fundamentals of the discrete molecule transform as 8a' and 7a'' modes. In addition, we expect some bands to arise from correlation splitting. The vibrational modes arising from stretching-type motions are located above *ca.* 350 cm^{-1} while those arising from bending or torsional type motions are located in the region below.

---

[19] I. Kawada and E. Hellner, *Angew. Chem.*, 1970, **82**, 390.

through 145 and 155 cm^{-1} in S_7 (a' and a'') to 202 cm^{-1} in S_6 (e_g). By contrast, the lowest i.r.-active fundamental is almost constant at 180—190 cm^{-1}.

Although the totally symmetric stretch shows little frequency change with ring size, the range of S–S stretching frequencies is much greater for S_7 than for either S_6 or S_8, probably associated with the much lower symmetry of S_7, and consequently less coupling than for the more highly symmetrical molecules.

The final assignment for S_7 is given in Table 1. The five polarised bands are clearly 5 of the 8 a' fundamentals. The remaining three are assigned by comparison with the assignment for S_6 and S_8. Each doubly degenerate vibration in these molecules should correspond to an a' and an a'' in S_7. In the absence of more conclusive evidence the a' vibrations are taken as those which are stronger in the Raman spectrum, while the a'' vibrations are taken as those which are stronger in the i.r. region. However, there is some doubt about the assignment of an a'' mode in the 200 cm^{-1} region. We prefer to attribute this mode to a shoulder at 242 cm^{-1} in the Raman spectrum, with the i.r. counterpart at 239 cm^{-1}. The doublet observed at 197 cm^{-1} may be due to correlation splitting.

In a preliminary study of the Raman spectrum of sulphur vapour,[9] a polarised band at 237 cm^{-1} was attributed to S_7. Our results confirm this assignment.

The force fields developed for S_8 [4,5] have been used to calculate frequencies for S_6.[13] The agreement with experimental frequencies was reasonably good, particularly when the force field was modified to give a higher value to the primary bending force constant. We used these force fields to calculate experimental frequencies for S_7 (Table 2). The agreement is only fair, undoubtedly because for S_6 and S_8, all the S–S bond lengths, S–S–S angles, and S–S–S–S torsions are equal. Only one primary force constant is therefore needed for the stretching, one for the bending, and one for the torsional co-ordinates. In S_7 the bond lengths and angles are not all equal, introducing errors into the calculated frequencies when only one force constant is used to describe each type of co-ordinate. Another error stems from the lack of accurate structural data on S_7. For our normal co-ordinate calculations, we used the data from the *X*-ray determination of the *xy* projection,[19] and assumed all the bond lengths were equal at 2·17 Å. However, quite small changes of geometry of the molecule gave relatively large changes in the frequencies of vibration, so a complete normal co-ordinate calculation must await a full *X*-ray diffraction study.

TABLE 2

Observed and calculated frequencies for S_7

		Calculated *		
Assignment	Observed	SVFF	SM	SMK
a'	517	603	481	530
	483	543	468	512
	402	484	454	471
	362	405	424	443
	268	275	276	280
	236	229	226	264
	184	135	133	156
	145	128	114	117
a''	510	602	457	516
	477	552	425	485
	397	449	422	448
	288	266	268	288
	242	225	228	266
	193	140	141	159
	155	103	103	152

* SVFF—Simple valence force field. SM—force field of Scott and McCullough.[4] SMK—force field of Scott, McCullough, and Kruse.[5]

EXPERIMENTAL

Cycloheptasulphur was prepared according to the method described by Schmidt *et al.*[14] The sample decomposed to amorphous sulphur (S_μ) at room temperature.

The Raman spectra were obtained using a Spex 1401 double monochromator, coupled to a Spectra Physics 125 He/Ne (632·8 nm) laser. Both the solid-state sample and the solution in carbon disulphide were cooled by passing dry air through a spiral in an acetone/solid CO_2 slush bath. No decomposition of the solid sample was observed, but some deterioration of the solution occurred. If more powerful laser lines were used, such as the Kr^+ lines at 647·1 and 568·2 nm from a C.R.L. 52 mixed-gas laser, a gradual conversion of S_7 to S_μ took place.

The i.r. spectra of Nujol mulls of S_7 were recorded on a Beckman IR11 spectrometer. The mull cells were mounted in evacuated cold cells and cooled using a cold finger containing liquid nitrogen.

A. R. is grateful to the British Council for a Fellowship. We wish to thank Professor I. R. Beattie and Dr. T. R. Gilson for helpful discussions.

[2/2085 *Received, 4th September,* 1972]