VIBRATIONAL SPECTRA AND STRUCTURES OF S₂(CH₃)₂ AND Se₂(CH₃)₂*

STEPHEN G. FRANKISS

Department of Chemistry, University College, London (Great Britain) and Mellon Institute, Pittsburgh, Pa. 15213 (U.S.A.)

(Received July 19th, 1968)

SUMMARY

The IR spectra between 33 and 4000 cm⁻¹ of $S_2(CH_3)_2$ and $Se_2(CH_3)_2$ in the vapour, liquid and solid states, and the Raman spectra with polarizations of $S_2(CH_3)_2$ (liquid) and $Se_2(CH_3)_2$ (liquid and solid) are reported. The data show that both molecules have non-planar CXXC (X = S or Se) skeletons with C_2 symmetry. A complete vibrational assignment for each molecule is presented.

INTRODUCTION

A recent analysis¹ of the microwave spectrum of dimethyl disulphide (S_2Me_2) has shown that, in the vapour state, it has a non-planar skeleton with C_2 symmetry. The Raman spectrum of liquid S_2Me_2 , however, has been interpreted on the basis of a cis planar skeleton with C_{2v} symmetry², although its vibrational spectrum has been subsequently reassigned on the basis of C_2 skeletal symmetry³. In view of this apparent discrepancy it seemed worthwhile re-examining the IR and Raman spectra of S_2Me_2 in detail, particularly since the related halides S_2Cl_2 and S_2Br_2 have C_2 symmetry in the liquid^{4,5} and gaseous⁶ states.

The dihedral angle of the S_2Me_2 skeleton in the vapour¹ is close to 90°, and similar dihedral angles have been reported in other disulphides⁷, which are attributed to the repulsion between the $3p\pi$ electrons of adjacent S atoms⁷. Less is known about the skeletal structures of diselenides, though the available evidence suggests⁷ that they too have dihedral angles that are close to 90°, indicating the importance of the interaction between the unshared pairs of $4p\pi$ electrons of adjacent Se atoms. In view of this lack of structural data for diselenides it seemed worthwhile examining the vibrational spectrum of dimethyldiselenide (Se₂Me₂) in order to obtain information about its skeletal structure in its various physical states.

^{*} This work was supported by the U.S. Army Research Office – Durham under grant ARO-D-31-124-G-735

EXPERIMENTAL

 S_2Me_2 , a colourless liquid, was obtained from B.D.H. and was purified by fractional distillation. Its vapour pressure at room temperature is ~ 22 torr. Se_2Me_2 was prepared by a standard procedure⁸ from the reaction between selenium, sodium formaldehydesulphoxylate and methyl sulphate in alkaline solution, and it was purified by repeated fractional distillation. It is an orange-coloured, foul smelling liquid with a vapour pressure of ~ 3 torr at ambient temperature. No proton-containing impurities could be detected from the proton resonance spectra of the samples of S_2Me_2 and Se_2Me_2 . Both compounds were conveniently handled in a conventional vacuum system.

IR spectra were recorded from 33 to 4000 cm^{-1} using Beckman IR-9 and IR-11 spectrophotometers. The compounds were studied in three forms: (a) in the vapour phase in a variable-path-length 10 m cell fitted with polyethylene or KBr windows, (b) as liquids in polyethylene and NaCl liquid cells, and as capillary films between KBr plates, and (c) as solids deposited from the vapour onto a KBr or polyethylene plate cooled by liquid nitrogen to roughly 100° K in a conventional low-temperature cell.

Raman spectra were obtained with a Cary Model 81 spectrophotometer using 6328 Å excitation from a Spectra-Physics 125 He-Ne laser. The compounds were studied as liquids in sealed melting point tubes, and as solids at about 140° K condensed from the vapour onto a probe in a novel low-temperature cell⁹. Qualitative depolarization measurements on the liquids were made using a half-wave plate between the laser beam and the sample, and a polaroid film between the sample and the monochromator.

RESULTS

The IR and Raman spectra of S_2Me_2 and Se_2Me_2 are given in Tables 1 and 2, respectively. Frequencies of typical bands should be accurate to $\pm 1 \text{ cm}^{-1}$ in the IR, and to $\pm 2 \text{ cm}^{-1}$ in the Raman spectrum.

The previously reported Raman spectrum² and IR spectrum (down to 500 cm⁻¹)¹⁰ of liquid S_2Me_2 are also included in Table 1. The earlier Raman spectrum agrees well with the present data except for the bands near 1400 cm⁻¹. The IR data obtained here are considerably more extensive than the low-resolution spectrum reported by Trotter and Thompson¹⁰. There is only fair agreement between the two sets of IR data.

An earlier unassigned low-resolution IR spectrum of liquid $\text{Se}_2\text{Me}_2^{11}$ is not listed in Table 2 since band frequencies were generally not given, and since the reported illustration of the spectrum shows only poor agreement with the more reliable data given in Table 2.

$S_2(CH_3)_2$ and $Se_2(CH_3)_2$

The low-temperature IR spectra in the range 400-4000 cm⁻¹ were obtained from both compounds as polycrystalline solids deposited on a KBr plate. When the compounds were deposited on a polyethylene plate, which was used to study the IR spectrum below 400 cm⁻¹, they appeared to form glasses and, although annealing was attempted, satisfactory crystallization was not obtained. Attempts were made to record the Raman spectrum of crystalline S_2Me_2 , but it could only be deposited as a glass giving no observable Raman scattering. Se_2Me_2 , on the other hand, was deposited as a polycrystalline solid in the Raman cell, and its spectrum in the range 50-600 cm⁻¹ is reported in Table 2^{*}. The discrepancies between the wavenumbers of corresponding IR and Raman bands in the low-frequency region of the low-temperature spectra of Se_2Me_2 probably arise from the different physical state of Se_2Me_2 in the two sets of measurements.

DISCUSSION

The skeleton CXXC, where X = S or Se, may have C_{2v} , C_{2h} or C_2 symmetry depending on whether the dihedral angle is 0°, 180° or some intermediate angle, respectively. The planar-trans model (C_{2h} symmetry) is centro-symmetric, and so it should show no coincidences between IR and Raman fundamentals, in contrast to the planar-cis model which may have 5 coincidences, and the non-planar model (C_2 symmetry) for which all six skeletal fundamentals are both IR- and Ramanactive. The planar-cis and non-planar models can be distinguished in their vibrational spectra only by the activity and state of polarization of the skeletal torsion, which is expected to be inactive in the IR and depolarized in the Raman spectrum of the non-planar model.

(a) Symmetry of the skeleton of S_2Me_2

The microwave spectrum of S_2Me_2 has shown¹ that, in the vapour phase, it has C_2 symmetry with a dihedral angle of 85°. The similarity between the IR spectra of S_2Me_2 in the vapour, liquid and solid states strongly indicates that it also has a non-planar skeletal structure in the liquid and solid states. From the vibrational spectra alone, we note that the observation of the skeletal torsion (near 100 cm⁻¹) in the IR spectra in all three states eliminates the planar-cis structure, while the planar-trans structure is inconsistent with the observation of several coincidences between strong Raman skeletal bands in the liquid and IR bands in all three states. The skeletal torsion appears to be depolarized, which is more consistent with the

^{*} I am very grateful to Dr. G. L. Carlson for recording the Raman spectrum of solid Se_2Me_2 , and for attempting to record the Raman spectrum of solid S_2Me_2 .

		-					
			IR				Assignment
pu	Present wo.	rk	Trotter and	Present work		-	
	liquid		I nompson"	vapour	liquid	solid (~100° K)	
ط	cm ⁻¹ I	μ	cm ⁻¹ I	cm ⁻¹ I	cm ⁻¹ I	cm ⁻¹ I	
	114 ms	dp'		106 m	117 m	W 140?a W	P ₁₃
'n	240 s	đ		242 m	241 m	1 242 ⁿ m	p ₁₁
dp?	274 ms	dp'		272 m	276 m	1 278ª m	V23
				489 w		· · · ·	$2 \times 242 = 484$?
ď	509 VS	d	517 m	509 mw	v 511 m	w 511 mw	, y ,
				wm 81c		•	
			533 VW				spurious?
	419 mm			WV 080			100+2×242 = 390
	MA 010			688 P		, 100 Million	$670 = 600 \pm 611$
£	60A VIS	£	500			Mill 600	
7		.	s 060	702 R	11 120	694 mw	V9 × V23
	743 w		741?				240+509 = 749
-				774 vw		169 W	272 + (513) = 785
				822 vw			962 - [140] = 822
				880 WV	,sh		106 + 272 + (513) = 891
	949 m	đ				951 vs	P8, P21
						957 VS	
		•		956] 。		959 VS	
			950 s	962) 7	955 V	s 962 vs	V7., V10
						968 m	278 + 691 = 9697
	1015 vw			1013 vw ∼1090 w,ł	,sh		2 × 509 = 1018 962 + [140] = 1102
•	1705	·		1001	1001		spurious?
	MA C071		MA 7611	MA 1071	1071		100 + 004 = 1203
				1217 VW 1303 P		1298 s	1671 = (ACA) + 717
• •			1298 s	1309 O m	1303 vs	1300 \$	2.0
				1317 R		1305 m	AT
	1311 mw	đ				1309 mw	9
	•					1314 mw	
	1379 w						$2 \times 694 = 1388$
	- - -		1410 s	1416P	1415 vc	1400 ve	9
2 			1710 0	7 77LT	21 AILI	ET 1771	F18

V.e. 1'	6 d	f(509)+955 = 1464	114 + 1426 = 1540	(240+1303 = 1543)	694+956 = 1650	(513) + 1309 = 1822	$2 \times 956 = 1912$		691 + 1303 = 1994		240 + 509 + 1303 = 2052	$3 \times 694 = 2082$	691 + 1430 = 2121	955+1303 = 2258	955 + 1430 = 2385	(513) + 694 + 1309 = 2516	$2 \times 1303 = 2606$		1303 + 1430 = 2739		$2 \times 1415 = 2830$	1415 + 1430 = 2845		V3, V16	t, t	· · · · · · · · · · · · · · · · · · ·	[134]+2986 = 3120	240 + 2986 = 3226	(513) + 2928 = 3441	694 + 2928 = 3622	694 + 2997 = 3691	$892 + 2 \times 1441 = 3774$	955+2915 = 3870	955+2986 = 3941
ഗ ഗ	I				¥				WV					¥	٨v				٨v		¥	≯		S	Э	: 3	:	37						
1432 1439					1663				1990					2260	2381				~2740		2811	2840		2913	7980	2991		~1220						
SV	<u>1</u>		mw,b						N		٨W		٨W	мm	W		٨v		٨٧		æ	E		٨S	U	5	mw.b	w h					M	: A
1430			~1540						1989		2048		2118	2255	2380		2600		2734		2817	2844		2915	2086		~ 3120	2002					3864	3934
J.	r	s	mw,b		ΜΛ	ΜΛ	WV		тw		٨W	ΨV	۸M	тw	тw	٨٧	٨٧		٨٧		E	E		SV .		o	mw.h	w h	οf	MA	MA	. MA		: 3
1441 01	1447 R	1458	~1536		1641	1830	1905	1994 P.	2000 0	2006 R	2057	2068	2134	2263	2381	2521	2610	2737 P)	2744 Q	2753 RJ	2835	2855	2921 P)	2928 Q	1X1 C262		~ 3140	-3740	1443	3624	1689	3778	3879	3942
1432 s																																		
dp?																					đ			đ	0.mp	'n								
E																					мш	¥		s	- 8	th The second	110-5111							
1426																					2815	2843		2913	1002	0000	0007							
																								đ	644	idn								
																								4 9	4	ר ר								
																								2914	1000	-027								

 $S_2(CH_3)_2$ and $Se_2(CH_3)_2$

93

RAMAD	N AND	IR SPECTRA O	F SeaMe								
Ramaı					IR						Assignment
liquid			solid (140°	(X	vapour		liquid		solid (100° K		
cm ⁻¹	I	ا م	cm ⁻¹	1	cm ⁻¹	1	cm ⁻¹	1	cm ⁻¹		
			54	E							lattice hands
001	. 1	0 m h	74	E	00				1140	3	
B	I	npr	139	* *	2	3				\$	814 • • • • •
			166	MA							lattice bands?
176	sm	đ	187	M			1807	w,sh	180	A	¹ 11
193	m,sh	dp?	201	W	184	M	190	W	193a	A	Pres Carl
286	SV	ď	285	vs	290	×	288	W	285a	mw	¹ 10
389	vw,sh	ı									$2 \times 193 = 386$
481	vw,sh										193 + 286 = 479
					572 P)						
			573	ms	577 Q 583 R	SIT	575	s	571	E	Va s
577	VS	a	581	ms					579	E	1' ₉
		•			~ 840	w,sh					80+184+577 = 8417
•					889 P				882	s	
892	∢	đ			894 Q	s	893	VS	887	E	78, 721
					899 R/				895	VS	
									897	S	
006	w,sh								<u>90</u> 6	SV	V7, V20
									606	E	
									913	S	
					0001∼	w,sh					894+[105] = 999
1145	Å				1147	w	1143	×	1135	×	$2 \times 575 = 1150$
					1265 P)				1249	u	, , , , , , , , , , , , , , , , , , ,
					1269 0	S	1259	VS	1254	VS	
					17.14 N						

J. Mol. Structure, 3 (1969) 89-101

TABLE 2

1265	E	- Д					1263	٤	1
							1269	E	- 11 ₈
							1272	æ	
•					1411	VS	1399	VS	1 ¹ 18
							1410	E	VB
CI4I	MH	apr {					1416	s	Va
		•	1429	S	1420	vs,sh	1425	s	V17
			1470	m,sh	1460	m,sh	1455	M	575 + 893 = 1468
1517	3		1530	wm	~ 1520	m,b			[99]+1420 = 1519
1780	Ŵ		1785	¥	1784	WW			$2 \times 893 = 1786$
1829			1844	M	1834	×			575 + 1259 = 1834
							2136	×	882 + 1254 = 2136
			2166	¥	2157	A	2155	W	893+1265 = 2158
2296	MA MA		2313	¥	2301	3			893 + 1411 = 2304
2508	M		2525	¥	2509	M	2513	w	$2 \times 1259 = 2518$
	-				2676	ΜΛ			1265 + 1411 = 2676
-2805	3		2830	E	2805	sm	2794	×	
	:						2800	3	7707
			2867	8					$2 \times 1429 = 2858$
2918	ms	Ċ	2937	VS	2920	VS	2913	s	;
[ł					2920	E	V3, V16
2996	≯	dp?	3011	s	2997	s	2988	шw	224,24
3008	w.sh				3008	s	3007	×	1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1
			3120	w,b	3100	W			[99]+(3002) = 3101
			3187	WA	3175	W			176 + (3002) = 3178
					3568	W			575 + (3002) = 3577
					3807	WV			893 + 2920 = 3813
					3896	W			893 + (3002) = 3895
Abbre a Fror	viation n glass	ns as for Table 1. s.							

liquid having a planar-cis structure, but skeletal torsions in the related halides S_2Cl_2 and S_2Br_2 have only weakly polarized Raman bands even though they are totally symmetric vibrations⁴, and so it appears quite likely that the skeletal torsion in S_2Me_2 may be only weakly polarized even though it is an *a* fundamental. Thus the overall evidence from its rotational and vibrational spectra strongly indicate that S_2Me_2 has a non-planar skeleton with C_2 symmetry in the vapour, liquid and solid states.

(b) Symmetry of the skeleton of Se_2Me_2

No microwave or diffraction data have been reported for Se_2Me_2 , and so a determination of its skeletal structure rests on its vibrational spectrum. The planartrans stucture can be eliminated in the liquid and the solid states by the observation of several coincidences between IR and Raman skeletal fundamentals. The planartrans structure can also be eliminated in the vapour phase by the observation of the IR band at 290 cm⁻¹ which is confidently assigned to the SeSe stretch.

The low-lying bands near 80 cm^{-1} in the vapour and 114 cm^{-1} in the solid are assigned to the skeletal torsion, which eliminates the planar-cis skeleton in these states. The liquid shows only a general IR absorption below 150 cm^{-1} , and so the absence of the skeletal torsion in the IR spectrum, which is expected to be close to 100 cm^{-1} does not provide good evidence for a planar-cis skeleton in the liquid. Likewise, the apparent depolarisation of the skeletal torsion in the Raman spectrum of the liquid (as with S_2Me_2) does not provide convincing evidence for a C_{2v} structure. The general similarity between the IR spectrum of the liquid with that of the solid and vapour strongly suggests that Se_2Me_2 has a similar skeletal structure having C_2 symmetry in all three states.

(c) Structural models

The microwave spectrum of S_2Me_2 has given its three principal moments of inertia, $I_A = 61.93$, $I_B = 179.479$ and $I_C = 196.679$ a.m.u. Å². The *B*-axis is colinear with the C_2 -axis of the molecule, and the *A*-axis is nearly parallel to the S-S bond¹. The Badger and Zumwalt asymmetry parameters¹² for this structure are

$$\rho = (A-C)/B = 2.0$$
 and $S = (2B-A-C)/(A-C) = -0.91$,

where A, B and C are the rotational constants associated with the principal moments. The S-value clearly characterizes the molecule as a symmetric spindle, and so its IR band contours in the vapour phase may be discussed in terms of the symmetric rotor approximation. In this approximation¹³, the A-type bands are expected to have "parallel-type" band contours, with a Q-branch intensity of about 20% of the whole band, and a P-R separation of about 15 cm⁻¹. The B- and Ctype bands are expected to have rather featureless contours with no prominent

$S_2(CH_3)_2$ and $Se_2(CH_3)_2$

P,Q,R band structure. There is, however, no symmetry requirement forbidding dipole moment changes at angles between the directions of the A and C axes. The a modes will therefore have B-type contours, but the b modes will have in general A/C hybrid band envelopes.

Accurate structural data for Se_2Me_2 are not known, but if it is assumed that Se_2Me_2 in the vapour has a similar geometry to S_2Me_2 then the *a* modes are expected to have rather featureless band contours in the vapour, while the *b* modes may have hybrid A/C band envelopes having a prominent P,Q,R structure with a P-R separation less than 15 cm⁻¹.

(d) Vibrational assignments

Although the skeletons of S_2Me_2 and Se_2Me_2 have C_2 symmetry, the overall molecular symmetry may be lower depending on the relative orientation of the methyl protons. We shall, however, assign the spectra of both molecules on the basis of overall C_2 symmetry, and so the fundamentals may be divided into thirteen of species *a* and eleven of species *b*. All twenty-four fundamentals are allowed in both the IR and Raman spectrum. In the Raman spectrum the *a* fundamentals are expected to be polarized, and the *b* fundamentals depolarized.

It is convenient further to divide the fundamentals in each molecule into (i) internal methyl vibrations, (ii) methyl torsions, and (iii) skeletal vibrations. The internal methyl vibrations are expected to lie above 800 cm^{-1} , while the methyl torsions and skeletal fundamentals should lie below 800 cm^{-1} .

(i) Internal methyl fundamentals

 S_2Me_2 . To a good approximation the CH stretches, deformations and rocks in S_2Me_2 can be described by two isolated CH₃ groups with local C_{3v} symmetry, having the "symmetric" and "antisymmetric" CH stretches near 2910 and 2990 cm⁻¹, respectively, the "symmetric" and "antisymmetric" CH deformations near 1310 and 1420 cm⁻¹, respectively, and the CH₃ rock near 950 cm⁻¹. The splitting of the "antisymmetric" CH stretch into 2983 and 2990 cm⁻¹ in the Raman spectrum of the liquid, the splitting of the "antisymmetric" CH deformation into 1419 and 1426 cm⁻¹ in the liquid, and the splitting of the rock into 949 and 955 cm⁻¹ is consistent with the presence of two isolated SCH₃ groups having C_s symmetry. The separation between the IR (1303 cm⁻¹) and Raman (1311 cm⁻¹) components of the "symmetric" CH deformation, however, requires an assignment on the basis of the overall molecular symmetry C_2 , though this results in several of the bands being assigned to more than one fundamental (Table 1).

On the basis of C_2 symmetry, we take the polarized Raman line 2913 cm⁻¹ as the *a* "symmetric" CH stretch v_3 , while the coincident IR band having a hybrid band contour in the vapour is assigned to the *b* "symmetric" CH stretch v_{16} . The four "antisymmetric" CH stretches can be assigned to only two transitions in the

liquid. We rather arbitrarily assign v_1 and v_{14} to 2990 cm⁻¹ and take 2983 cm⁻¹ as v_2 and v_{15} .

The polarized Raman band 1311 cm^{-1} is a clear choice for v_6 the *a* "symmetric" CH deformation, leaving the IR band at 1303 cm^{-1} in the liquid, which has a hybrid band contour in the vapour, as the *b* "symmetric" CH deformation v_{19} . The four "antisymmetric" CH deformations must be assigned to the Raman band a. 1419 and 1426 cm⁻¹ and the IR at 1415 and 1430 cm⁻¹ in the liquid. The counterparts of the IR bands in the vapour have hybrid band envelopes, which suggests that they are the *b* CH deformations v_{17} and v_{18} . The Raman bands 1426 and 1419 cm⁻¹ appear to be depolarized and are almost coincident with the IR bands, and so they too may be *b* CH deformations, but since the *a* "antisymmetric" CH deformations are expected to be only weakly polarized and to be close to the *b* "antisymmetric" CH deformations, we tentatively assign the Raman bands at 1426 and 1419 cm⁻¹ to the *a* "antisymmetric" CH deformations v_4 and v_5 , respectively.

The 949 cm⁻¹ Raman and the 955 cm⁻¹ IR bands are the only two that can be confidently assigned to the four CH₃ rocks. The Raman band is polarization sensitive and, on crossing the polarizer, it is reduced in intensity and shifts to 953 cm⁻¹. Thus the 949 cm⁻¹ band appears to be polarized, while the Raman counterpart of the 955 cm⁻¹ IR band is probably depolarized. A possible candidate for a third CH₃ rock is the very weak IR band at 880 cm⁻¹ in the vapour, but this assignment is not particularly satisfactory since this absorption is not observed in the liquid or solid. For lack of any other suitable bands we assign all four CH₃ rocks to the bands near 955 cm⁻¹, taking v_7 and v_{20} as 955 cm⁻¹, and v_8 and v_{21} as 949 cm⁻¹ in the liquid. This assignment is consistent with the force constant calculations of Scott et al.³, who have predicted that all four CH₃ rocks in S₂Me₂ lie in the range 940–960 cm⁻¹.

 Se_2Me_2 . The assignments of the CH stretches and CH deformations in Se_2Me_2 , which are summarized in Tables 2 and 3, follow the assignment of S_2Me_2 , and need not be discussed further. Two Raman bands at 900 and 892 cm⁻¹ in the liquid can be assigned to CH₃ rocks and, since the latter is polarized, it must be one of the two *a* CH₃ rocks. The 892 cm⁻¹ Raman band is coincident with that at 893 cm⁻¹ in the IR, but its vapour-state counterpart at 894 cm⁻¹ has a hybrid band envelope which suggests that the IR band is a *b* fundamental. Thus the Raman and the IR bands near 893 cm⁻¹ in the liquid probably arise from different transitions, and so three of the CH₃ rocks are at 900, 893 and 892 cm⁻¹ in the liquid. The weak IR band at 840 cm⁻¹ in the vapour is a possible candidate for the fourth CH₃ rock but, since it is not observed in the liquid or the solid, this assignment seems rather unsatisfactory. It is more likely that the fourth CH₃ rock is near 900 cm⁻¹, and so, following S₂Me₂, we assign 900 cm⁻¹ to v_7 and v_{20} , leaving 892 cm⁻¹ as v_8 and 893 cm⁻¹ as v_{21} in the liquid.

$S_2(CH_3)_2$ AND $Se_2(CH_3)_2$

TABLE 3

C <u></u>	No.	Schematic	Frequency (c	:m ⁻¹)
specie	S	description	S2Me2 (liquid)	Se _s Me _s (liquid)
a	1	antisym. CH stretch	2990	3008
	2	antisym. CH stretch	2983	2996
	3	sym. CH stretch	2913	2918
	4	antisym. CH defn.	1426	1415
	5	antisym. CH defn.	1419	1415
	6	sym. CH defn.	1311	1265
	7	CH ₃ rock	955	900
	8	CH ₃ rock	949	892
	9	XC stretch	694	577
	10	XX stretch	509	286
	11	XXC bend	240	176
	12	CH ₃ torsion	[134]	[99]
	13	skeletal torsion	117	100
Ь	14	antisym. CH stretch	2990	3008
	15	antisym. CH stretch	2983	2996
	16	sym. CH stretch	2915	2920
	17	antisym. CH defn.	1430	1420
	18	antisym. CH defn.	1415	1411
	19	sym. CH defn.	1303	1259
	20	CH ₃ rock	955	900
	21	CH ₃ rock	949	893
	22	XC stretch	691	575
	23	XXC bend	274	193
	24	CH ₃ torsion	[134]	[99]

FUNDAMENTALS OF X_2Me_2 (X = S, Se)

[] from combination tone.

(ii) Methyl torsions

The methyl torsions in S_2Me_2 and Se_2Me_2 have not been observed directly. Three combination tones in S_2Me_2 which are assigned using a methyl torsion are the IR bands near 3140, 1090 and 822 cm^{-1} , which give 140 and 134 cm⁻¹ as approximate values for the methyl torsions in the vapour and liquid, respectively. The vapour value agrees moderately well with the value (150 cm^{-1}) calculated using the microwave structure and value of V_3 $(1.6\pm0.1 \text{ kcal mole}^{-1})^1$. In Se₂Me₂ the IR bands near 3120, 1530 and 1000 cm⁻¹ are assigned using a methyl torsion, which give 105 and 99 cm⁻¹ as approximate values for the methyl torsions in the vapour and liquid, respectively.

(iii) Skeletal fundamentals

The six fundamentals associated with the CXXC skeleton in each molecule are divided into four of species a and two of species b. The a fundamentals are expected to be polarized, and the b fundamentals depolarized, in the Raman spectrum.

 S_2Me_2 . The three polarized Raman lines 694, 509 and 240 cm⁻¹ are three of the *a* fundamentals. The fourth *a* fundamental is surely the lowest Raman band at 114 cm⁻¹, even though it appears to be depolarized, since the lowest fundamental is expected to be the torsion. The highest *a* skeletal fundamental 694 cm⁻¹ can be described as the *a* SC stretch v_9 , since it is close to the SC stretches in SMe₂ (692 and 742 cm⁻¹)¹⁴. 509 cm⁻¹ is a clear choice for the SS stretch v_{10} , since it is close to the SS stretch in S₂Cl₂ (540 cm⁻¹)^{4,5} and in S₂Br₂ (534 cm⁻¹)^{4,5}. This leaves 240 cm⁻¹ as the *a* CSS bend v_{11} .

The apparently depolarized 274 cm^{-1} band is one of the two *b* skeletal fundamentals, and its proximity to v_{11} indicates that it is the *b* CSS bend v_{23} . The second *b* fundamental, which is a SC stretch, has been assigned² to the Raman band at 743 cm⁻¹, but this seems unlikely since 743 cm⁻¹ is weak in the Raman spectrum and it is absent in the IR spectrum, particularly since it can be satisfactorily assigned to a combination tone (Table 1). Two observations suggest that the *b* SC stretch is very close to the *a* SC stretch at 694 cm⁻¹. Firstly, in determining the polarization of the 694 cm⁻¹ band, it was observed that on crossing the polarizer the band maximum shifted from 694 to 693 cm⁻¹, which indicates that this Raman band consists of a polarized component 694 cm⁻¹ and a less polarized or depolarized component at slightly lower frequency. Secondly, the IR band centered at 690 cm⁻¹ in the vapour has a hybrid band envelope, which indicates that at least part of the band is due to a *b* fundamental. We therefore assign the 694 cm⁻¹ IR band in the liquid to the centre of the *a* SC stretch v_{22} .

 Se_2Me_2 . The assignments of the skeletal fundamentals of Se_2Me_2 closely follow those of S_2Me_2 (see Table 3), and so they need not be discussed in any detail. The four *a* fundamentals are clearly assigned to 577 (SeC stretch, v_9), 286 (SeSe stretch, v_{10}), 176 (CSeSe bend, v_{11}) and 100 cm⁻¹ (skeletal torsion, v_{13}). The two *b* fundamentals are taken as 575 (SeC stretch, v_{22}) and 193 cm⁻¹ (CSeSe bend, v_{23}) in the liquid. The two SeC stretches appear to be resolved in the solid into 572 and 580 cm⁻¹, although this may be due to factor group splitting.

(e) Discussion of the skeletal fundamentals

A few comments about the "skeletal" fundamentals in molecules of the type YXXY where $Y = CH_3$, Cl or Br, and X = S or Se, are perhaps worth noting as they may assist the assignments of more complicated disulphides and diselenides. In each of the six molecules that have been studied the two YX stretches lie very close together, the largest separation being about 15 cm^{-1} in $S_2Cl_2^{4,5}$. The XX stretches are good group frequencies, shifting only slightly with change of $Y^{4,5}$. In the three Se_2Y_2 molecules, the SeSe stretches lie in the very narrow range $289 \pm 3 \text{ cm}^{-1}$. These observations suggest that there is little coupling between the

$S_2(CH_3)_2$ AND $Se_2(CH_3)_2$

three skeletal stretches, which is perhaps not surprising as the skeletal bond angles appear to be close to 90°. Finally, in all six molecules the skeletal torsion is found to be rather sensitive to the molecular environment⁴.

ACKNOWLEDGEMENTS

I am very grateful to Prof. F. A. Miller for granting me use of the spectroscopic facilities at Mellon Institute during the tenure of a Visiting Research Fellowship in the summer of 1967, and for his interest in this work. I am indebted to I.C.I. for a Research Fellowship at University College.

REFERENCES

- 1 D. SUTTER, H. DREIZLER AND H. D. RUDOLPH, Z. Naturforsch., 20A (1965) 1676.
- 2 H. GERDING AND R. WESTRIK, Rec. Trav. Chim., 61 (1942) 412.
- 3 D. W. SCOTT, H. L. FINKE, M. E. GROSS, G. B. GUTHRIE AND H. M. HUFFMAN, J. Am. Chem. Soc., 72 (1950) 2424.
- 4 S. G. FRANKISS, J. Mol. Structure, 2 (1968) 271.
- 5 P. J. HENDRA AND P. J. D. PARK, J. Chem. Soc. (A), (1968) 908.
- 6 E. HIROTA, Bull. Chem. Soc. Japan, 31 (1958) 130.
- 7 S. C. ABRAHAMS, Quart. Rev., 10 (1956) 407.
- 8 M. L. BIRD AND F. CHALLENGER, J. Chem. Soc., (1942) 570.
- 9 G. L. CARLSON, Spectrochim. Acta, 24A (1968) 1519.
- 10 I. F. TROTTER AND H. W. THOMPSON, J. Chem. Soc., (1946) 481.
- 11 G. BERGSON, Arkiv. Kemi, 13 (1958) 11.
- 12 R. M. BADGER AND L. R. ZUMWALT, J. Chem. Phys., 6 (1938) 711.
- 13 S. L. GEHARD AND D. M. DENNISON, Phys. Rev., 43 (1933) 197.
- 14 J. R. ALLKINS AND P. J. HENDRA, Spectrochim. Acta, 22 (1966) 2075.