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THE RAMAN SPECTRA OF VARIOUS BIS (PERFLUOROETHYL) SULPHIDES,
SELENIDES, AND TELLURIDES

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SUMMARY

The vibrational spectra of $(C_2F_5)_2S_x$ ($x=2,3,4$), $(C_2F_5)_2Se_x$ ($x=1,2,3$), $(C_2F_5)_2Te_x$ ($x=1,2$) and C_2F_5SeCl are reported and tentative assignments proposed.

INTRODUCTION

Perfluoroalkyl derivatives of sulphur [1] and selenium [2,3] have been reported over the past twenty years; preparative methods and chemistry of these compounds have been reviewed [4,5]. Perfluoroalkyl derivatives of tellurium have been more recently synthesised [6,7,8,9]. Raman investigations have been reported for $(CF_3)_2Se_x$ ($x=1,2$) [10,11], related species CF_3SeX ($X=H$ [10], D [10], CN [10,11], Cl [10,11], Br [10,11], CH_3 [11]) and $(CF_3)_2S_x$ ($x=1,2$) [12]. Analysis of the Raman spectra of higher perfluoroalkyl derivatives (i.e. $(C_2F_5)_2M_x$) has been carried out for the related perfluoroethyl halides [13]. Over the past several years, studies on the reactions of sulphur, selenium, and tellurium polycations [14] with tetrafluoroethylene [8,15,16] has yielded a ready synthesis of compounds of the type $(C_2F_5)_2M_x$ ($M=S$ ($x=2-4$), Se ($x=2,3$), Te ($x=1,2$)). This paper reports the vibrational spectra of these compounds. Infrared spectra have been reported for $(C_2F_5)_2Se_x$ ($x=1,2$) [3], C_2F_5SeCl [3], $(C_2F_5)_2Te$ [8,9] and $(C_2F_5)_2Te_2$ [8].

EXPERIMENTAL

Raman spectra were obtained using a Spex Ramalab RS2 spectrometer equipped with a spectra-physics 164 2W Ar-Kr laser as the exciting source ($5145\overset{\circ}{\text{A}}$, $6471\overset{\circ}{\text{A}}$). Scattered radiation was collected at 90° to the incident light. The spectral slit width

was 4 cm^{-1} unless otherwise specified. Depolarization ratios were determined by turning the electric vector of the scattered light through 90° by using a half-wave plate. Except for weak, broad lines and overlapping bands, ratios were obtained by measuring the area under the peaks. Spectra were calibrated using the appropriate lines from carbon tetrachloride and indene samples; frequencies are believed accurate to $\pm 2 \text{ cm}^{-1}$, except for shoulders, weak and broad lines where the uncertainty is much greater. Low temperature Raman spectra were obtained using a variable temperature assembly (Harney Miller type). The neat liquid samples were contained in sealed melting point capillaries.

Infrared spectra were obtained in a 10 cm gas cell (pressures ranging .1-150 torr) fitted with potassium bromide windows (Harshaw Chemicals) on a Beckman IR-12 and Perkin-Elmer 457 spectrometer and calibrated using a polystyrene film. Frequencies are believed accurate to $\pm 2 \text{ cm}^{-1}$.

Bis(perfluoroethyl) di-, tri- and tetra-sulphides were obtained as products from the reaction of octasulphur bis(hexafluoroarsenate) and tetrafluoroethylene [15], bis(perfluoroethyl) di- and tri-selenides from the reaction of octaselenium bis(hexafluoroarsenate) and tetrafluoroethylene [16], bis(perfluoroethyl) mono- and di-tellurides from the reaction of tetratellurium bis(hexafluoroarsenate) and tetrafluoroethylene [8]. Bis(perfluoroethyl) monoselenide and perfluoroethyl selenyl chloride were prepared by a slight modification of the reported methods [3]. A high degree of purity (ca. 95%) was obtained for all but two compounds by preparative gas chromatography using a 1/4" by 10' stainless steel tubing packed with 10% Kel-F wax (Applied Science Laboratories) on Chromasorb W. $(\text{C}_2\text{F}_5)_2\text{Se}_3$ was found to contain 8% $(\text{C}_2\text{F}_5)_2\text{Se}_2$ by v.p.c.. $\text{C}_2\text{F}_5\text{SeCl}$ was purified by trap to trap distillation. Its purity was established by ^{19}F n.m.r. (95%) and its spectrum [84.4ppm (CF_3); 97.5ppm (CF_2)] was consistent with previous results [3]. Bis(perfluoroethyl) triselenide and ditelluride were unstable towards heat and light. $(\text{C}_2\text{F}_5)_2\text{Se}_3$ decomposed at room temperature depositing elemental selenium, $(\text{C}_2\text{F}_5)_2\text{Te}_2$ decomposes in the laser beam at room temperature and spectra could only be obtained at very low temperatures and high gain. All species studied

remained unchanged over a period of two years when stored in the dark at low temperatures (<0°C).

RESULTS AND DISCUSSION

Stereochemistry of polysulphides have been reviewed [17,18,19] and polysulphides of the general formula X_2S_y can exist as 2 (y=2), 3 (y=3) and 6 (y=4) stable rotational and optical isomers. Substitution of the X group by C_2F_5 results in the possibility of additional rotational isomers arising from rotation about the C-S bond as evidenced in the Raman spectra of dialkyl disulphides by the presence of several S-S stretches [20-25]. C-S stretching frequencies were also found to depend on the particular molecular conformation [20,24,25]. Complexity of a similar nature would therefore be expected in the Raman spectra of the analogous bis(perfluoroethyl) sulphides, selenides, and tellurides. Spectra of these molecules recorded at high resolution and low temperature (i.e. -130°C, spectra of liquid samples remained unchanged on solidification) did not exhibit evidence for these isomers. Either one conformer is present for these species or the M-M stretch is the same for all isomers.

The symmetry class of the molecules $(CF_3)_2Se$ [26], $(CF_3)_2Se_2$ [27], $(CF_3)_2S_2$ [12], C_2F_5X (X=Cl,Br,I) [13] and CF_3SeX [10,11] which are related to those to be studied are either C_2 or C_s . Replacement of a CF_3 group by a C_2F_5 group in these species will result in the same or lower symmetry. While most of our assignments are satisfactory, there may be mixing of vibrational modes such that shorthand descriptions (i.e. C-M, M-M stretches, etc.) are sometimes not justified. In all cases the number of vibrational modes expected exceed those observed.

(1) $C_2F_5S_2C_2F_5$. The vibrational spectrum of $(C_2F_5)_2S_2$ is tabulated with tentative assignments (Table 1). A representative Raman spectrum is also given (Fig. 1c). Carbon-fluorine stretching vibrations have been established to be in the 1400-1000 cm^{-1} range [28] and are strong in the infrared but weak in the Raman.

TABLE 1

Vibrational Spectra of $(C_2F_5)_2S_2$, $(C_2F_5)_2S_3$ and $(C_2F_5)_2S_4$

$(C_2F_5)_2S_2$		$(C_2F_5)_2S_3$		$(C_2F_5)_2S_4$		Assignments (Tentative)
Infrared (I)	Raman (I)	Infrared (I)	Raman (I)	Infrared (I)	Raman (I)	
1332* (vs)	1338 (5)	1333 (vs)	1330 (3)	1332 (s)	1328 (1)	C_2F_5 str.
1280 (w)						CF_4 ?
1232 (vs)	1218 (9)	1234 (s)	1215 (5)	1229 (s)	1213 (1)	C_2F_5 str.
		1193 (w)	1156 (1)	1194 (w)		
1168 (vs)	1172 (1)	1163 (m)	1148 (1)	1162 (m)	1150 (<1)	C_2F_5 str.
				1147 (m)		
1124 (vs)	1114 (4)	1117 (s)	1113 (2)	1114 (s)	1108 (1)	C_2F_5 str.
		1007 (w)	993 (sh)		1025 (<1)	
964 (wsh)	966 (sh)	965 (s)	970 (3)	966 (m)	964 (sh)	C-C str.
950 (vs)	946 (2)	953 (s)	954 (sh)	952 (s)	950 (1)	
886 (w)					890 (1)	
818 (w)	820 (1)					
750 (s)	750 (39)	751 (m)	752 (53)	750 (s)	751 (21)	CF_3 deformation
694 (m)	728 (sh)		728 (sh)	672 (w)	723 (sh)	
649 (m)	649 (9)	648 (w)	647 (5)	649 (m)	645 (2)	C_2F_5 deformation
630 (m)	632 (8)	630 (w)	630 (3)	630 (m)	627 (2)	
596 (w)	594 (6)	594 (vw)	594 (3)	550 (w)	593 (1)	
		549 (vw)	549 (6)		549 (4)	
548 (m)	549 (38)	519 (vw)	516 (57)	518 (w)	503 (33)	sym. S-S str.
		495 (w)	490 (13)		514 (sh)	asym. S-S str.
		471 (w)				
455 (sh)	456 (sh)	458 (vw)	455 (6)	459 (w)		asym. C-S str.

TABLE 1. continued

$(C_2F_5)_2S_2$		$(C_2F_5)_2S_3$		$(C_2F_5)_2S_4$		Assignments
Infrared (I)	Raman (I)	Infrared (I)	Raman (I)	Infrared (I)	Raman (I)	(Tentative)
434 (vw)	433 (38)	435 (vw)	435 (12)		446 (23)	sym. S-S str.
400 (w)	402 (28)	400 (w)	403 (22)		433 (sh)	sym. C-S str.
385 (w)		385 (vw)			400 (7)	C_2F_5 rock
377 (vw)		376 (vw)				
	363 (12)		363 (7)		365 (3)	C_2F_5 rock
	319 (24)		320 (sh)		315 (sh)	
	308		311 (sh)			
	290 (30)		299 (24)		303 (8)	C_2F_5 rock
	278 (sh)					
	226 (12)		231 (30)		234 (22)	
	211 (sh)		221 (sh)		215 (19)	
	200 (29)		210 (br)			
	181 (sh)		198 (sh)		187 (16)	
			180 (br)		164 (br)	skeletal deform.?
			166			
			148 (sh)			
	132 (98)		134 (46)		134 (sh)	skeletal deform.?
	111 (100)		100 (100)		105 (100)	torsion?

* All frequencies in cm^{-1}

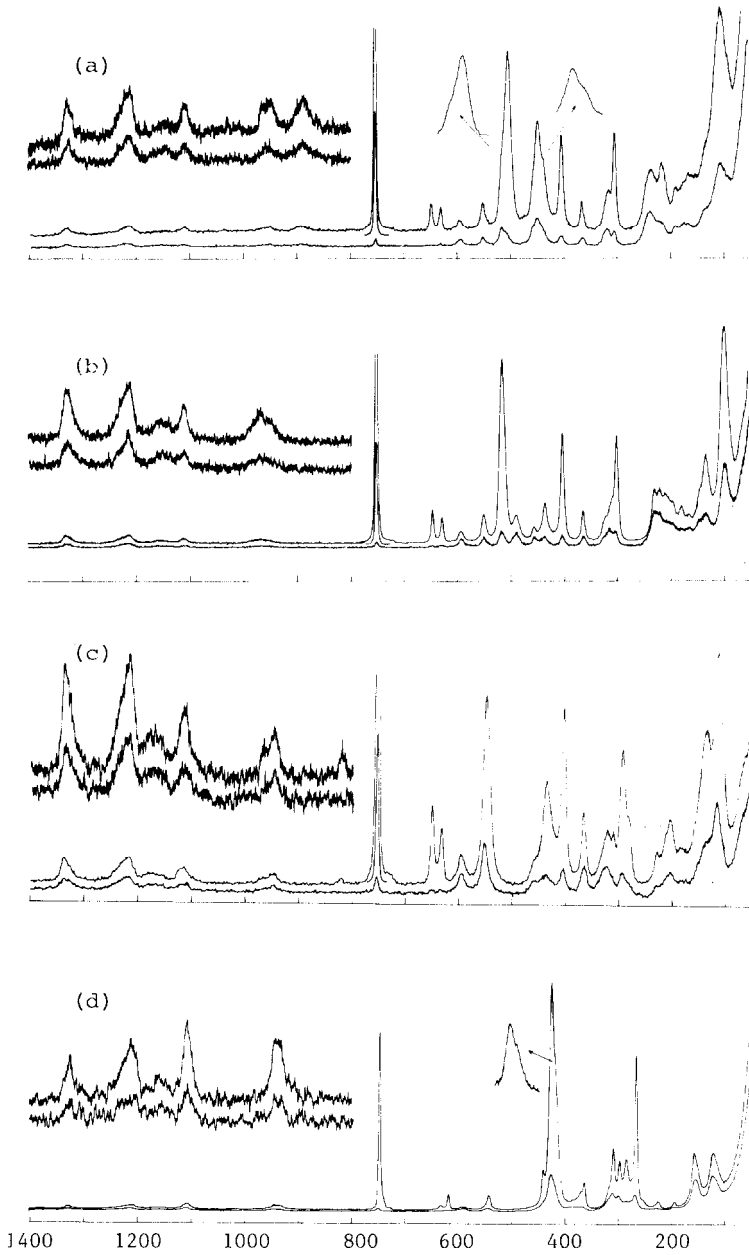


Figure 1. Polarized and depolarized Raman spectra of
 (a) $(\text{C}_2\text{F}_5)_2\text{S}_4$, (b) $(\text{C}_2\text{F}_5)_2\text{S}_3$, (c) $(\text{C}_2\text{F}_5)_2\text{S}_2$
 and (d) $\text{C}_2\text{F}_5\text{SeCl}$.

Four weak, broad lines observed at 1338, 1218, 1172, 1114 cm^{-1} are assigned as C-F stretching modes of the C_2F_5 group. A band observed at 1280 cm^{-1} in the infrared but absent in the Raman is possibly a CF_4 impurity peak. The frequency range 850-1000 cm^{-1} is designated as the C-C stretching region although assignment of this mode has not been well established [28]. However, assignments for the C-C stretch have been reported for dialkyl disulphides [22] and fluorocarbons [29] and fall within this frequency range. Peaks at about 950 cm^{-1} have been observed for $\text{C}_2\text{F}_5\text{Cl}$ [30], $\text{C}_2\text{F}_5\text{X}$ [13] (X=Cl,Br,I) but are absent for $(\text{CF}_3)_2\text{S}_2$ [12]. Therefore the bands observed at 966, 946 cm^{-1} probably have a strong contribution from a C-C stretch. One of the strongest Raman bands in the spectra of CF_3 containing compounds [10,11,12] is a CF_3 deformation mode at about 750 cm^{-1} . Therefore, we assign the peak at 750 cm^{-1} in the Raman to this vibrational mode. The strong band at 750 cm^{-1} in the infrared is assigned as the asymmetric CF_3 deformation consistent with results reported by Wahi for $(\text{CF}_3)_2\text{Se}_2$ [31]. The peaks at 649, 632 and 594 cm^{-1} fall in the region of C_2F_5 deformations and their assignment is consistent with invariance of these bands in the series of compounds studied.

The region incorporating the C-S and S-S vibrational modes is of interest for perfluoroalkyl sulphides. The S-S stretching frequency has been observed over a small frequency range (500-550 cm^{-1}) for a number of related compounds (Table 2.). Therefore, it is reasonable to assign the strong, polarized band at 549 cm^{-1} as the S-S symmetric stretch. The C-S stretching vibration has been well characterized for alkyl sulphides and is in the frequency range 620-730 cm^{-1} [23,24,33]. However, in the heavier fluorocarbon analogues the C-S stretching frequency is shifted to lower wave numbers (e.g. C-S stretch in $(\text{CF}_3)_2\text{S}_2$ [12]; sym. 446 cm^{-1} , asym. 450 cm^{-1}). Therefore, we assign the C-S symmetric stretch to the polarized band at 433 cm^{-1} . The weak band at 456 cm^{-1} may either be a C_2F_5 rocking mode or an asymmetric C-S stretch.

CF_3 and C_2F_5 rocking modes have been assigned in related systems [12,13,38] and are intense polarized bands. Two strong, polarized peaks observed at 402 cm^{-1} and 290 cm^{-1} are assigned as C_2F_5 rocking modes. We note that these intense bands are invariant

TABLE 2

S-S stretching frequencies in Disulphides

Compound	S-S stretch(cm^{-1})	Reference
HSSH	509	32
CH_3SSCH_3	509	33
CF_3SSCF_3	536	12
$\text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$	508, 523	20
$\text{C}_2\text{F}_5\text{SSC}_2\text{F}_5$	549	this work
$\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$	523	24
BrSSBr	534	34, 35
ClSSCl	540	34, 35
$\text{C}_6\text{F}_5\text{SSC}_6\text{F}_5$	486	35, 36
S_2F_2	623	37

for $(\text{C}_2\text{F}_5)_2\text{S}_2$, $(\text{C}_2\text{F}_5)_2\text{S}_3$ and $(\text{C}_2\text{F}_5)_2\text{S}_4$. The strong intensity, low frequency bands at 132 and 111 cm^{-1} are tentatively assigned as skeletal deformation and torsion modes. The remaining peaks are unassigned.

(2) $\text{C}_2\text{F}_5\text{S}_3\text{C}_2\text{F}_5$. The Raman spectrum is given in figure 1b and the vibrational spectrum with their tentative assignments is given in Table 1. Assignments for the C_2F_5 portion of the spectrum are the same as for $(\text{C}_2\text{F}_5)_2\text{S}_2$.

By analogy with $(\text{C}_2\text{F}_5)_2\text{S}_2$ the symmetric C-S stretch is assigned to the band at 435 cm^{-1} . The weak band at 455 cm^{-1} may contain contributions from the asymmetric C-S stretch and/or a C_2F_5 rocking mode. Symmetry requires that a non linear planar X_3 system contain a symmetric and asymmetric X-X stretching mode [39]. Therefore, the two bands at 516 and 490 cm^{-1} are assigned as the symmetric and asymmetric S-S stretches respectively on the basis of their relative intensity and depolarization ratios. The lower S-S asymmetric stretch assignment is consistent with other related trisulphides (Table 3).

TABLE 3

Some S-S stretches in trisulphides and tetrasulphides

Compound	S-S stretch (cm ⁻¹)-Raman			Reference
	sym., asym.			
H ₂ S ₃	488,470			40
(C ₆ F ₅) ₂ S ₃	484			36
(C ₂ H ₅) ₂ S ₃	499,486			41
(CCl ₃) ₂ S ₃	510,474			42
(CH ₃) ₂ S ₃	513,480			42
(C ₂ F ₅) ₂ S ₃	516,490			this work

	asym. S-S str.	sym. terminal S-S str.	central S-S str.	
(C ₂ F ₅) ₂ S ₄	514	503	446	this work
H ₂ S ₄	484	484	454	40

	*S-S str. (unassigned)			
(C ₆ F ₅) ₂ S ₄	475			36
(C ₂ H ₅) ₂ S ₄	486,438			41
(CCl ₃) ₂ S ₄	503,430			42
(CH ₃) ₂ S ₄	487,441			42
Na ₂ S ₄	481,448,424			43

*The particular S-S stretches (i.e. sym., asym., terminal and central) were not assigned.

(3) C₂F₅S₄C₂F₅. The Raman spectrum is given in figure 1a and the vibrational spectrum with tentative assignments is given in Table 1. The C₂F₅ portion of the spectrum is the same as in the previous compounds.

The C-S and S-S stretching region of (C₂F₅)₂S₄ is simple. We expect a central S-S stretch, a symmetric terminal S-S stretch and an asymmetric S-S stretch [39] for an isolated non planar

S_4 unit. These stretches have been assigned in related tetrasulphides (Table 3). Therefore the strong, polarized band at 503 cm^{-1} is assigned to the symmetric terminal S-S stretch and the shoulder at 514 cm^{-1} is attributed to the asymmetric terminal S-S stretch. By analogy with H_2S_4 [40], the central S-S stretch is assigned to the weaker band at 446 cm^{-1} . This band incorporates a shoulder at 433 cm^{-1} which is assigned to the symmetric C-S stretch.

The S-S stretching frequency decrease, as the sulphur chain lengthens, is consistent with other data on various polysulphides reported by Steudel [19].

(4) C_2F_5SeCl . A representative Raman spectrum is given in figure 1d. Vibrational frequencies and tentative assignments are found in Table 4. Assignments for the frequency range $1400-500\text{ cm}^{-1}$ remain unchanged from previous compounds. (i.e. $(C_2F_5)_2S_x$ ($x=2,3,4$)). An additional weak band observed at 438 cm^{-1} for the bis(perfluoroethyl) selenides and tellurides is probably a C_2F_5 deformation.

A very strong, polarized band at 424 cm^{-1} which incorporates a weak shoulder at 418 cm^{-1} is assigned as the Se-Cl stretch. This is consistent with the Se-Cl stretch assignment for gaseous $SeCl_2$ (415 cm^{-1}) [44] and for CF_3SeCl [10] which has two bands at $425, 419\text{ cm}^{-1}$ assigned as Se- ^{35}Cl , Se- ^{37}Cl stretches. Absence of this band in bis(perfluoroethyl) mono-, di- and tri-selenides is consistent with this Se-Cl stretching assignment. The C-Se stretching mode is assigned to the band at 306 cm^{-1} . C-Se stretches have been assigned at higher frequencies for CF_3SeCl (335 cm^{-1}) and related molecules [10,11], and another possible C-Se stretch assignment is the shoulder band at 362 cm^{-1} . Bands at $368, 282, 266$ and 223 cm^{-1} are assigned as C_2F_5 rocking modes and are observed for bis(perfluoroethyl) mono-, di- and tri-selenides. Peaks at $154, 118\text{ cm}^{-1}$ are assigned as possible skeletal deformations, bending or torsion modes. The remaining peaks are unassigned.

(5) $(C_2F_5)_2Se$. A representative Raman spectrum of bis(perfluoroethyl) monoselenide is given in figure 2b. Vibrational frequencies and tentative assignments are in Table 4.

TABLE 4. continued

C_2F_5SeCl		$C_2F_5SeC_2F_5$		$C_2F_5Se_2C_2F_5$		$C_2F_5Se_3C_2F_5$		Assignment
Raman (I)	IR (I)	Raman (I)	IR (I)	Raman (I)	IR (I)	Raman (I)	Raman (I)	
533 (sh)								
541 (4)	538 (m)	542 (8)	540 (m)	543 (7)	533 (w)	542 (2)		
438 (8)		437 (3)	432 (w)	440 (1)		456 (1)		C_2F_5 deform.
424 (100)	425 (m)					437 (1)		Se-Cl str.
418 (sh)								
368 (sh)	390 (w)	371 (25)		366 (12)		365 (5)		C_2F_5 rock
362 (2)		365 (25)						C_2F_5 rock
		346 (7)						sym. C-Se str.
317 (sh)		333 (13)				316 (sh)		asym. C-Se str.
306 (14)		324 (25)		322 (32)		306 (23)		sym. C-Se str.
295 (14)				307 (32)				
						287 (27)		asym. Se-Se str.
282 (18)		282 (31)		288 (46)		275 (38)		sym. Se-Se str.
266 (28)		258 (100)		283 (sh)				C_2F_5 rock
				254 (44)				C_2F_5 rock
		253 (100)		244 (36)		245 (31)		C_2F_5 rock
223 (2)		220 (8)		221 (7)		220 (5)		C_2F_5 rock
192 (1)								

TABLE 4. continued

C_2F_5SeCl	$C_2F_5SeC_2F_5$	$C_2F_5Se_2C_2F_5$	$C_2F_5Se_3C_2F_5$	Assignment
Raman(I)	IR(I)	Raman(I)	IR(I)	Raman(I)
154 (27)	153 (sh) 136 (38)	150 (30)	142 (12)	skeletal deformation?
118 (40)		139 (9) 127 (25) 91 (100)	109 (84) 88 (100)	Torsion?

* All frequencies in cm^{-1} .

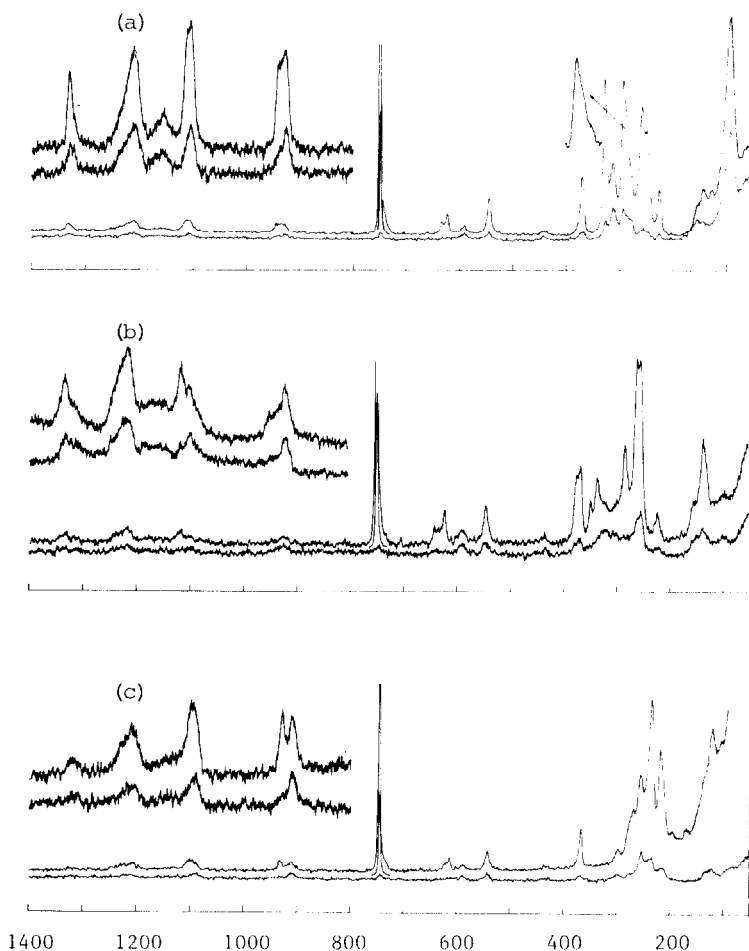


Figure 2. Polarized and depolarized Raman spectra of
 (a) $(\text{C}_2\text{F}_5)_2\text{Se}_2$, (b) $(\text{C}_2\text{F}_5)_2\text{Se}$, and
 (c) $(\text{C}_2\text{F}_5)_2\text{Te}$.

Two strong peaks at 371, 365 are assigned to C_2F_5 rocking and C-Se stretching modes respectively. The assignment of the C-Se stretch is consistent with results for $(\text{CF}_3)_2\text{Se}$ (364 cm^{-1}) [10,11]. The band at 333 cm^{-1} is assigned as an asymmetric C-Se stretch in agreement with that reported for $(\text{CF}_3)_2\text{Se}$ (339 cm^{-1}) [10,11]. Assignment of weaker bands in this region is uncertain.

(6) $(C_2F_5)_2Se_2$. A representative Raman spectrum is given in figure 2a. Vibrational frequencies and tentative assignments are in Table 4. The symmetric and asymmetric C-Se stretching vibrations are assigned to the peaks at 322 and 307 cm^{-1} respectively. The lower frequency asymmetric C-Se stretch is consistent with results reported for $(CF_3)_2Se_2$ [10,11,31]. A strong polarized peak at 288 cm^{-1} is assigned to the Se-Se stretch and is in agreement with the observed Se-Se stretches found for a variety of diselenides (Table 5), but in disagreement with

TABLE 5

Se-Se stretching frequency in Diselenides

Compound	Se-Se str.(cm^{-1})	Reference
$CF_3SeSeCF_3$	245	10
$CF_3SeSeCF_3$	318	11
$CF_3SeSeCF_3$	287	31,34
$C_2F_5SeSeC_2F_5$	288	this work
$CH_3SeSeCH_3$	286	33,45
$(C_6F_5)_2Se_2$	280	46
di-n-butyl diselenide	293	24
Se_2Cl_2	292,289	34,35
Se_2Br_2	286,290	34,35

that reported by Marsden [10] and Clase et al [11]. The 254 cm^{-1} peak in the spectrum of $(C_2F_5)_2Se_2$ appears in the spectra of the other bis(perfluoroethyl) selenides and is therefore reasonably assigned as a C_2F_5 rocking mode and it is probable that Marsden's peak at 245 cm^{-1} is a CF_3 rocking mode, rather than the Se-Se stretch, consistent with the results of Clase et al [11]. However, the latter authors [11] assign the Se-Se stretch to a weak band at 318 cm^{-1} in the region where we assign C-Se stretching modes for $(C_2F_5)Se_x$ ($x=2,3$).

(7) $C_2F_5Se_3C_2F_5$. A representative Raman spectrum is given in figure 3. Vibrational frequencies and tentative assignments are found in Table 4. The C-Se symmetric and asymmetric stretching modes are assigned to peaks at 306 and 316 cm^{-1} respectively. The symmetric and asymmetric selenium stretching modes are assigned to the peaks at 275 and 287 cm^{-1} respectively based on polarization data. The 287 cm^{-1} peak may possibly contain a C_2F_5 rocking mode consistent with a polarized band observed at 282 cm^{-1} for $(C_2F_5)_2Se$.

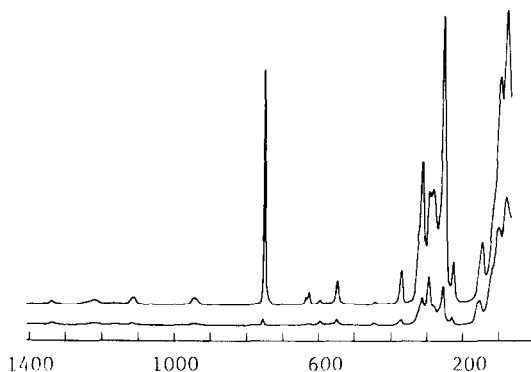


Figure 3. Polarized and depolarized Raman spectra of $(C_2F_5)_2Se_3$.

(8) $(C_2F_5)_2Te$. A representative Raman spectrum is given in figure 2c. Vibrational frequencies are tabulated and tentative assignments given in Table 6.

Due to lack of vibrational assignments for perfluoroalkyl derivatives of tellurium, our assignments are based on comparisons with alkyl derivatives of tellurium. Examination of C-S, C-Se and C-Te stretching assignments for $(CH_3)_2S, Se$ [47], $(CF_3)_2S$ [12], $(CF_3)_2Se$ [10,11], $(CH_3)_2Se_2$ [45], $(CH_3)_2S_2$ [33], $(CF_3)_2Se_2$ [10,11] $(CF_3)_2S_2$ [12], $(CH_3)_2Te$ [47] and $(CH_3)_2Te_2$ [48] lead to the assignment of the C-Te symmetric stretches in $(C_2F_5)_2Te$ to bands at about 300 cm^{-1} . Several probable bands are observed in this region (i.e. 295 , 276 and 267 cm^{-1}) and assignment is uncertain. Strong bands at 251 , 231 and 213 cm^{-1} are assigned as possible

TABLE 6

Vibrational Spectra of $(C_2F_5)_2Te_x$ ($x=1,2$)

$(C_2F_5)_2Te$		$(C_2F_5)_2Te_2$		Assignment
Raman (I)	Infrared (I)*	Raman (I)	Infrared (I)*	
1318 (3) *	1315 (s)		1317 (s)	} C-F stretching
	1297 (wsh)			
	1281 (wsh)		1281 (w)	
1210 (11)	1229 (s)		1223 (s)	
	1147 (m)		1139 (m)	
1096 (10)	1099 (m)		1099 (m)	
927 (4)	933 (wsh)			} C-C stretching
909 (5)	913 (s)		913 (s)	
			861 (w)	
742 (37)	741 (m)	742 (45)	739 (m)	CF ₃ deformation
729 (sh)				} C ₂ F ₅ deformation
619 (4)				
611 (1)	609 (w)		607 (w)	
585 (2)				
540 (5)	531 (w)		531 (w)	
432 (2)				
365 (10)				
295 (11)				
276 (sh)				
267 (sh)		258 (25)		C ₂ F ₅ rocking or C-Te stretching?
251 (80)		242 (sh)		
231 (100)		237 (40)		C ₂ F ₅ rocking
213 (80)		219 (5)		
193 (sh)				
		190 (100)		Te-Te stretch
166 (37)		166 (17)		
117 (81)				skeletal deformation?
100 (14)				torsion?

* The Infrared spectra of $(C_2F_5)_2Te_x$ ($x=1,2$) were obtained from previous work [8].

** All frequencies in cm^{-1} .

C_2F_5 rocking modes. A band at 117 cm^{-1} is assigned as a skeletal deformation mode.

(9) $(C_2F_5)_2Te_2$. Vibrational frequencies obtained with their tentative assignments are given in Table 6.

By comparison with results obtained for $(C_2F_5)_2Te$, the probable assignment for the peak observed at 258 cm^{-1} is either to a C-Te symmetric stretch or a C_2F_5 rocking mode. One of the strongest bands in the spectrum at 190 cm^{-1} is assigned as the Te-Te stretch consistent with Te-Te stretch assignments for $(CH_3)_2Te_2$ (189 cm^{-1}) [48] and a series of diaryl ditellurides ($167\text{-}187\text{ cm}^{-1}$) [49]. Bands at 237 and 219 cm^{-1} are possibly C_2F_5 rocking modes.

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REFERENCES

- 1 G.A.R. Brandt, H.J. Emeléus and R.N. Haszeldine, J. Chem. Soc. (1952) 2198.
- 2 J.W. Dale, H.J. Emeléus and R.N. Haszeldine, J. Chem. Soc., (1958) 2939.
- 3 N. Welcman and H. Regev, J. Chem. Soc., (1965) 7511.
- 4 R.E. Banks, "Fluorocarbons and Their Derivatives", MacDonald, London (1970), 174-187 and appendix.
- 5 A. Haas, "Gmelin Handbuch", Band 9, Teil 1; Band 12, Teil 2; Verlag Chemie, Weinheim, 1973.
- 6 T.N. Bell, B.J. Pullman and B.O. West, Aust. J. Chem., 16 (1963) 722.
- 7 R.J. Lagow, L.L. Gerchman, R.A. Jacob and J.A. Morrison, J. Amer. Chem. Soc., 97 (1975) 518.
- 8 C.D. Desjardins, H.L. Paige, J. Passmore and P. Taylor, J. Chem. Soc. (Dalton), (1975) 488;

- H.L. Paige and J. Passmore, *Inorg. Nucl. Chem. Letters* 9 (1973) 277.
- 9 M.L. Denniston and D.R. Martin, *J. Inorg. Nucl. Chem.* 37 (1975) 1871.
- 10 C.J. Marsden, *J. Fluorine Chem.* 5 (1975) 401.
- 11 P.K. Wahi, H.J. Clase and D.R.L. Bomford, in press.
- 12 H.A. Carter, C.S-C Wang, J.M. Shreeve, *Spectrochim. Acta* 29A (1973) 1479.
- 13 O. Risgin and R.C. Taylor, *Spectrochim. Acta* 12 (1959) 1036.
- 14 R.J. Gillespie and J. Passmore, "Adv. in Inorg. Chem. and Radiochem."; H.J. Emeléus, A.G. Sharpe - eds., Academic Press (London) 17 (1975) 49.
- 15 H.L. Paige and J. Passmore, *Inorg. Chem.* 12 (1973) 593.
- 16 C.D. Desjardins and J. Passmore, *J. Chem. Soc. (Dalton)* (1973) 2314.
- 17 R. Rahman, S. Safe and A. Taylor, *Quart. Rev.* 24 (1970) 208.
- 18 O. Foss, "Organic Sulphur Compounds", N. Kharasch-ed., Pergamon Press (London) 1 (1961) 75.
- 19 R. Steudel, *Angew. Chem. Internat. Edit.* 14 (1975) 655.
- 20 H. Sugeta, A. Go and T. Miyazawa, *Bull. Chem. Soc. Japan*, 46 (1973) 3407.
- 21 D.W. Scott, H.L. Finke, J.P. McCullough, M.E. Gross, R.E. Pennington and G. Waddington, *J. Amer. Chem. Soc.*, 74 (1952) 2478.
- 22 H. Sugeta, *Spectrochim. Acta.* 31A (1975) 1729.
- 23 E.J. Bastian, Jr. and R.B. Martin, *J. Phys. Chem.*, 77 (1973) 1129.
- 24 K.G. Allum, J.A. Creighton, J.H.S. Green, G.J. Minkoff and L.J.S. Prince, *Spectrochim. Acta.* 24A (1968) 927.
- 25 S.K. Freeman, "Application of Raman Spectroscopy", Amer. Chem. Soc. Audio Course, Washington, D.C., (1973) 96.
- 26 C.J. Marsden and G.M. Sheldrick, *J. Molec. Str.* 10 (1971) 405.
- 27 C.J. Marsden and G.M. Sheldrick, *J. Molec. Str.* 10 (1971) 419.
- 28 J.K. Brown and K.J. Morgan, "Advan. Fluorine Chem.", 4 (1965) 253.
- 29 E.L. Pace, A.C. Plaush and H.V. Samuelson, *Spectrochim. Acta.*, 22 (1966) 993.
- 30 J.R. Nielson, C.Y. Liang, R.M. Smith and D.C. Smith, *J. Chem. Phys.* 21 (1953) 383.
- 31 P.K. Wahi, M. Sc. thesis, Memorial University (1973).

- 32 F. Fehér, *Angew. Chem.* 59 (1947) 33.
- 33 S.G. Frankiss, *J. Molec. Str.*, 3 (1969) 89.
- 34 P.J. Hendra and P.J.D. Park, *J. Chem. Soc. (A)*, (1968) 908.
- 35 S.G. Frankiss, *J. Molec. Str.*, 2 (1968) 271.
- 36 M.E. Peach, *Int. J. Sulphur Chem.*, 8 (1973) 27.
- 37 R.D. Brown and G.P. Pez, *Spectrochim. Acta* 26A (1970) 1375.
- 38 P.J. Hendra, R.A. Johns, C.T.S. Miles, C.J. Vear and A.B. Burg *Spectrochim. Acta.*, 26A (1970) 2169.
- 39 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, New York, 1963.
- 40 H. Wieser, P.J. Krueger, E. Muller and J.B. Hyne, *Can. J. Chem.* 47 (1969) 1633.
- 41 F. Fehér, G. Krause and K. Vogelbruch, *Chem. Ber.* 90 (1957) 1570.
- 42 F. Fehér and H.J. Berthold, *Chem. Ber.* 88 (1955) 1634.
- 43 F.P. Daly and C.W. Brown, *J. Phys. Chem.*, 79 (1975) 350.
- 44 G.A. Ozin and A. Vander Voet, *Chem. Comm.* (1970) 896.
- 45 W.H. Green and A.B. Harvey, *J. Chem. Phys.*, 49 (1968) 3586.
- 46 R.T. Poole, Ph.D. thesis, Memorial University (1973).
- 47 J.R. Allkins and P.J. Hendra, *Spectrochim. Acta* 22 (1966) 2075.
- 48 C.W. Sink and A.B. Harvey, *J. Molec. Str.*, 4 (1969) 203.
- 49 W.R. McWhinnie and P. Thavornnyutikarn, *J. Organometal. Chem.* 35 (1972) 149.