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SPECTROSCOPIC INVESTIGATIONS OF CF_3Se-DERIVATIVES

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SUMMARY

The vibrational spectra of CF_3SeH, CF_3SeD, CF_3SeCl, CF_3SeBr, CF_3SeCN, CF_3SeCl_3, $(CF_3)_2Se$ and $(CF_3Se)_2$ are reported, and vibrational assignments presented. N.m.r. parameters for a wide range of CF_3Se-derivatives are tabulated.

INTRODUCTION

Although CF_3Se-derivatives were first prepared nearly twenty years ago,[1] they have been investigated remarkably little by modern physical techniques. This communication presents the results of a study of the vibrational spectra of eight CF_3Se- compounds, together with their n.m.r. parameters and some observations on equilibria and exchange processes followed by n.m.r. spectroscopy.

EXPERIMENTAL

Infrared spectra were run in the gas phase (except for CF_3SeCl_3) at pressures in the range 0.5 - 150 mm Hg, in a 10 cm cell using CsBr windows on a Perkin Elmer 457 instrument. Calibration was achieved from appropriate lines in the spectra of CO, CO_2, H_2O, and polythene.

Frequencies are believed accurate to ± 3 cm^{-1}, except perhaps for the very weakest, broad bands.

Raman spectra were run in the liquid phase, (except for CF_3SeCl_3) in sealed capillaries on a Coderg PHl machine equipped with a He-Ne laser operating at 6328 Å. Qualitative depolarization ratios were determined using a half-wave plate, between the laser and sample, to rotate the direction of the electric vector by 90°. For some weak, broad lines, and for some overlapping bands, satisfactory measurements could not be made. The spectra were calibrated using appropriate lines in the spectra of carbon tetrachloride and indene; frequencies quoted are believed accurate to ± 2 cm^{-1}, except for broad, weak bands, where the uncertainty may be 5 cm^{-1}.

N.m.r. spectra were variously recorded on Perkin Elmer R10 and R12B machines, and Varian HA100 and XL100 instruments. The precision of the chemical shifts and coupling constants quoted depends on the instrument used; most chemical shifts are believed precise to within 0.02 ppm, except for $CF_3SeTl\ Me_2$, where the uncertainty is 0.1 ppm. Coupling constants are believed accurate to within 0.3 Hz if a decimal figure is quoted, but to within 2 Hz otherwise. The chemical shifts quoted in Table 7 refer to solutions roughly 20% by volume in CCl_3F. Solvent shifts of up to 1 ppm were observed using other solvents such as deuteroacetone or bromine.

CF_3SeH and CF_3SeD were prepared using a slight modification of the original procedure,[1] to give essentially quantitative yields. The appropriate hydrogen bromide was condensed onto $Hg(SeCF_3)_2$, left at -78°C for 30 minutes, and the volatile products purified in the vacuum system. CF_3SeCl was prepared by the reaction of chlorine on $Hg(SeCF_3)_2$ at room temperature,[1] and purified in the vacuum system. CF_3SeBr was prepared by mixing $(CF_3Se)_2$ and bromine in equimolar ratios at room temperature. CF_3SeCN was prepared by streaming CF_3SeBr through a column packed with AgCN. CF_3SeCl_3 was prepared by mixing $(CF_3Se)_2$ and Cl_2 in the molar ratio 1:3.5, then the residual chlorine was removed by pumping. To record the infrared spectra of CF_3SeCl_3, the compound was prepared on the window of a low-temperature cell, though the spectra were recorded at room temperature. $(CF_3)_2Se$ and $(CF_3Se)_2$ were prepared following standard procedures.[1]

RESULTS AND DISCUSSION

1. Vibrational Spectra

(a) CF_3SeH and CF_3SeD

Molecules of the type CF_3SeX possess, at most, C_s symmetry, and thus twelve fundamental vibrations, distributed as eight A' and four A''. However, it has been found in this work that the observed spectra can often be analysed assuming local C_{3v} symmetry for the CF_3Se- group. This approximation, which is found to be particularly appropriate when X is H or D, reduces the number of normal modes to nine.

There are six modes involving the CF_3Se- group only, of which three are of A_1, three of E symmetry. These may be described in an approximate shorthand way as:

ν_1	The symmetric CF_3 stretch	A_1
ν_2	The symmetric CF_3 deformation	A_1
ν_3	The C-Se stretch	A_1
ν_4	The asymmetric CF_3 stretch	E
ν_5	The asymmetric CF_3 deformation	E
ν_6	The CF_3 rock	E

The remaining three modes involve the motion of the X atom:

ν_7 The Se-X stretch

ν_8 The C-Se-X bend

ν_9 The torsion of CF_3 about Se-X bond.

All nine modes are active in both the Raman and infrared effects. As numbered above, $\nu_1 - \nu_3$ and $\nu_7 - \nu_8$ are expected to be Raman polarized, the remainder depolarized. The molecules are fairly heavy; for CF_3SeH, the rotational constant B is calculated as about 2000 MHz, or 0.067 cm^{-1}, assuming molecular dimensions similar to those determined by recent electron diffraction studies of CF_3Se-compounds.[2] Thus little information can be obtained from the gas-phase infrared band shapes, using the equipment available for this work.

The observed vibrational spectra of CF_3SeH and CF_3SeD are given in Table 1. Figure 1 shows representative Raman spectra of the liquid phase. The vibrations involving the H or D atom are readily assigned; substitution of D for H drastically lowers the frequency of two modes, but has little eff on the rest of the spectrum. The small magnitude of the changes introduced by substituting D for H indicates that the assumption of local $\underline{C}_{3v}$ symmetry i.e. ignoring the presence of the X atom, is not unreasonable. The ratio ν(Se - H/ν(Se - D) is found to be 1.391, slightly less than $\sqrt{2}$, as is generally observed.

The vibrations of the CF_3- group are now well established. Modes $\nu_1 - \nu_6$ fit the pattern to be expected by analogy with, e.g. CF_3H[3], CF_3Br and CF_3I[4], and CF_3PH_2 and CF_3AsH_2.[5] Although the carbon-selenium stretching frequency in CH_3SeH is observed at 582 cm^{-1},[6] a much lower value is expected for the compounds studied here, since the heavy CF_3- group has effectively increased the reduced mass of the carbon atom. The strong Raman band at 334 cm^{-1} is assigned as ν_3, a frequency similar to the analogous value of 350 cm^{-1} found for CF_3Br.[4] The deformation ν_8 is

TABLE 1

Vibrational Spectra of CF_3SeH and CF_3SeD

Raman (cm^{-1})				Infrared (cm^{-1})				Assignment
CF_3SeH		CF_3SeD		CF_3SeH		CF_3SeD		
2336	p,m			2340	w,			ν_7
				2285	w,	2292	w	$\nu_1 + \nu_4$
				2235	vw	2245	w	$2\nu_1$
				1905	w	1907	w	$\nu_2 + \nu_4$
				1865	w	1855	w	$\nu_1 + \nu_2$
		1 680	p,m			1687	w	ν_7
				1650	vw			$\nu_1 + \nu_5$
				1530	vw			$\nu_2 + \nu_8$
				1450	vw			$\nu_3 + \nu_4$
				1270	w	1265	mw	$\nu_2 + \nu_5$
1160	dp,vw,vbr	1155	dp,vw,br	1170	vs	1171	vs	ν_4
1105	p,w,br	1102	p,w	1125	vs	1126	vs	ν_1
1075	dp,vw,br	1072	vw,br	1080	m	1080	m	$\nu_2 + \nu_3$
				925	w,br			
788	dp,w,br			785	s			ν_8
744	p,s	742	p,s	748	s	750	s	ν_2
		598	w,br			595	w	ν_8
533	dp,w,br	519	dp,w,br	530	w	518	mw	ν_5
334	p,s	332	p,s	335	w	335	m	ν_3
286	dp,w	284	dp,w					ν_6

ν_9 not observed
Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; p, polarized; dp, depolarized

apparently depolarized, although predicted to be polarized. Nevertheless, its assignment cannot be doubted, in view of its behaviour on substitution of D for H. This point is discussed in more detail below.

The torsional mode ν_9 was not observed in these studies, nor can its frequency be deduced convincingly from combination bands. A gas-phase

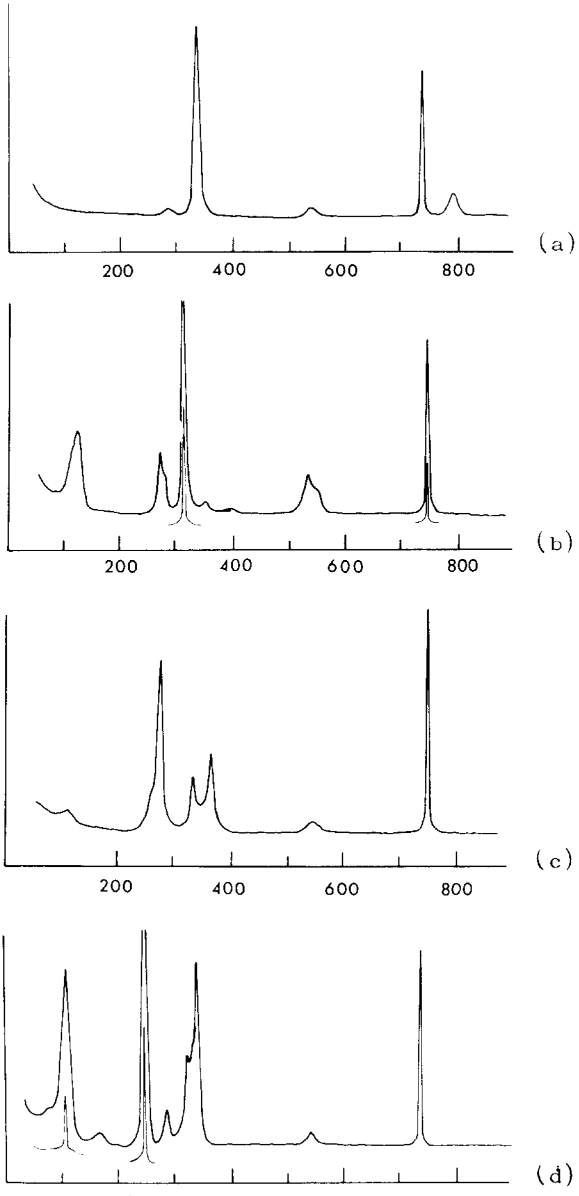

Figure 1. Representative Raman spectra of liquid samples of (a) CF$_3$S
(b) CF$_3$SeCN, (c) CF$_3$SeCF$_3$, (d) CF$_3$SeSeCF$_3$.
Lower trace shows most intense peaks recorded at lower gain
Frequencies in cm^{-1}.

infrared study of CF_3SH showed the torsional mode to lie at 175 cm^{-1}[7], but unfortunately that spectral region could not be studied in this work.

TABLE 2

Vibrational Spectra of CF_3SeCl and CF_3SeBr

Raman (cm^{-1})				Infrared (cm^{-1})				Assignment	
CF_3SeCl		CF_3SeBr		CF_3SeCl		CF_3SeBr			
				2360	w			$2\nu_4$	
				2280	vw	2265	vw	$\nu_1 + \nu_4$	
				1911	vw			$\nu_2 + \nu_4$	
				1854	vw			$\nu_1 + \nu_2$	
						1797	w		
				1347	vw,br	1334	w		
				1274	w			$\nu_2 + \nu_5$	
						1230	w,sh	$\nu_1 + \nu_8$	
				1179	vs	1180	vs	ν_4	
1098	p,vw,br			1110	vs	1110	vs	ν_1	
				1091	mw			$\nu_5 + \nu_7 + \nu_8$	
				1073	w,sh			$\nu_2 + \nu_3$	
				1024	vw	1028	w	$\nu_2 + \nu_6$	
						850	vw	$\nu_2 + \nu_8$	
				848	vw			$2\nu_7$	
743	p,ms	745	p,m	745	m	740	s	ν_2	
535	dp,w,br	545	vw,br	536	vw	528	vw	ν_5	
425	p,s			430	mw			ν_7	^{35}Cl
419	p, sh							ν_7	^{37}Cl
		342	p,m			335	mw, sh	ν_7	
335	p,m	324	p,m	337	w	320	m	ν_3	
278	p,m	266	p,s					ν_6	
129	dp,mw,br	111	dp,m					ν_8	

ν_9 not observed

(b) CF_3SeCl and CF_3SeBr

The observed spectra of these two compounds are presented in Table 2. The same system of numbering the fundamental modes is used as was given above for CF_3SeH. The assignment of the fundamental frequencies for the two molecules follows directly from that of CF_3SeH. The simplifying assumption of local $\underline{C}_{3v}$ symmetry for the CF_3Se- group appears to hold well, with the one exception that the rocking mode ν_6 appears polarized in the Raman effect, rather than depolarized as predicted for a degenerate $\underline{E}$ vibration. The appearance of several moderately intense bands in the infrared spectrum in the C-F stretching region is taken not as a breakdown of this assumption, but rather as an example of the familiar resonance process, whereby a combination mode may gain intensity if its frequency sum lies near that of a very intense fundamental.

In the Raman spectrum of liquid CF_3SeCl, the Se-Cl stretching vibration is just resolved into two components expected for ^{35}Cl and ^{37}Cl. A first-order calculation of the isotopic splitting, based on the usual reduced mass formula and ignoring the existence of several isotopes of selenium, gives a value of 7 cm^{-1}, in good agreement with the (poorly-determined) experimental value of 6 cm^{-1}. The frequency found for the symmetric Se-Cl stretch in gaseous $SeCl_2$ is 415 cm^{-1},[8] similar to that reported here. The Raman spectrum of CF_3SeBr shows two bands of similar intensity in the region of the C-Se stretching frequency. It is not clear which to assign as the "C-Se stretch" and which as the "Se-Br stretch", evidently there will be appreciable mixing of these two modes. Although 342 cm^{-1} may appear rather a high frequency for a Se-Br stretching motion, compared with the values of 257 and 260 cm^{-1} found for the $\underline{B}$ and $\underline{A}$ modes of Se_2Br_2,[9,10] in CF_3SeCl the Se-Cl stretch lies at 425 cm^{-1}, appreciably higher than the $\underline{B}$ and $\underline{A}$ modes in Se_2Cl_2, namely 353 and 360 cm^{-1} [9,10].

The lowest frequency band observed in the Raman spectra of these molecules is assigned as the bending vibration ν_8 rather than the torsional

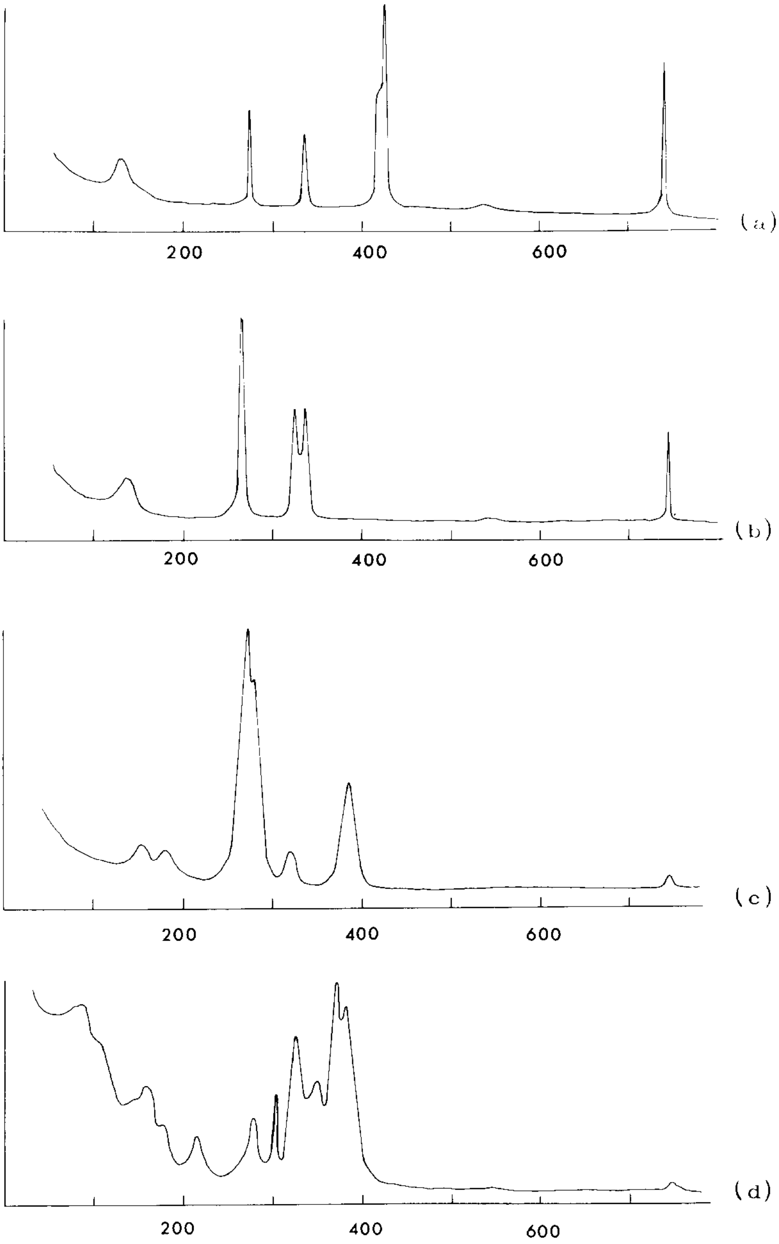

Figure 2. Representative Raman spectra of (a) liquid CF$_3$SeCl, (a) liquid CF$_3$SeCl, (b) liquid CF$_3$SeBr, (c) CF$_3$SeCl$_3$ in THF soln, (d) solid CF$_3$SeCl$_3$. Frequencies in cm^{-1}.

mode ν_9, despite being apparently depolarized, for several intuitive reasons. It is possible for a totally symmetric mode to have a depolarization ratio insignificantly lower than the limiting value of 0.75 predicted for non-symmetric modes, and such behaviour has in fact been observed for $(CH_3)_2Se$.[11] Measurements of the depolarization ratios of bands at comparatively low frequency are subject to large error using double-monochromator instruments, since they lie on a sloping background due to the Rayleigh scattering.
The torsional mode would be expected at a frequency appreciably lower than 130 cm^{-1}. Although unambiguous direct observations of these vibrations are very rare; the gas-phase infrared spectrum of CF_3OF shows a weak absorption at 56 cm^{-1}, attributed to the torsional mode.[12] Finally a frequency of 129 cm^{-1} for the skeletal deformation in CF_3SeCl is reasonable by comparison with the value of 153 cm^{-1} observed for gaseous $SeCl_2$.[8]

(c) CF_3SeCN

The observed spectra of CF_3SeCN are set out in Table 3. For this molecule the spectra are too complex to be classified using local $\underline{C}_{3v}$ symmetry for the CF_3Se- group. Presumably this breakdown is caused by the more advantageous possibilities of mechanical coupling presented by the greater number of vibrations in CF_3SeCN, than in CF_3SeH. The fifteen normal modes are divided under $\underline{C}_s$ symmetry into ten of $\underline{A}'$, and five of $\underline{A}''$ symmetry. They may be described as

ν_1	C ≡ N stretch	ν_9	CF_3 rock
ν_2	CF_3 asymmetric stretch	ν_{10}	C-Se-C bend
ν_3	CF_3 symmetric stretch	ν_{11}	CF_3 asymmetric stretch
ν_4	CF_3 symmetric deformation	ν_{12}	CF_3 asymmetric deformation
ν_5	CF_3 asymmetric deformation	ν_{13}	Se-C-N bend out-of-plane
ν_6	Se-C(N) stretch	ν_{14}	CF_3 rock
ν_7	Se-C-N bend in-plane	ν_{15}	CF_3 torsion
ν_8	Se-C(F_3) stretch		

TABLE 3 : Vibrational Spectra of CF_3SeCN

Raman (cm^{-1})		Infrared (cm^{-1})		Assignment
2264	p,w	2290	w	$\nu_2 + \nu_3$
2170	p,m	2190	vw,	ν_1
		1940	vw	$\nu_2 + \nu_4$
		1850	vw	$\nu_3 + \nu_4$
		1280	w	$\nu_4 + \nu_5$
1182	dp,w,br	1200	vs	ν_2
		1165	m,sh	ν_{11}
1093	p,w,br	1102	vs	ν_3
1059	vw	1065	s	$\nu_4 + \nu_8$
748	p,s	751	s	ν_4
545	w,sh,br	540	m	ν_5
533	p,mw,br			ν_6 and ν_{12}
399	vw, br	390	w	ν_7
356	w,br	355	w	ν_{13}
316	p,s	314	w	ν_8
282	w,sh			ν_9
273	dp,m			ν_{14}
122	dp,m,br			ν_{10}

ν_{15} not observed

ν_1 - ν_{10} are A', and expected to be Raman-polarized, while the A'' modes ν_{11} — ν_{15} are depolarized. Most of the assignment follows directly from that for CF_3SeH, and from literature spectra of CH_3SCN[13] and CH_3SeCN[14]. The C≡N stretching mode is seen at a frequency similar to that of other cyanides, which indicates that the molecule is a true cyanide CF_3SeCN rather than an isocyanide CF_3SeNC, for which the analogous frequency would be much lower than the 2170 cm^{-1} found here. It is not clear whether the A' or A'' asymmetric stretching mode will be more intense in the infrared effect, and unfortunately the Raman frequencies do not correspond very closely with those in the infrared. This difference is probably associated with the difference of phase studied by the two methods; similar behaviour has been observed in CF_3S- derivatives.[15] The distinction in Table 3 between ν_2 and ν_{11} was made on the basis of a normal coordinate analysis, which will be reported elsewhere.

TABLE 4

Vibrational Spectra of CF_3SeCl_3

(a) Infrared solid (cm^{-1})

1194	sh	749	s
1175	vs	362	s,br
1120	s	335	sh
1093	vs	311	sh
1077	sh		

(b) Raman solid (cm^{-1})

1159	vw,br	277	m
745	w	213	m
383	s	181	vw
369	s	166	m
345	m,br	148	vw
325	s	108	w,br
302	m	83	m

(c) Raman solution in THF (cm^{-1})

1065	dp,vw,br	281	p,s
745	p,w	269	p,vs
384	p,m	181	?dp,w
319	p,mw	154	?dp,w

(d) CF_3SeCl_3

The observed spectra of CF_3SeCl_3 are given in Table 4. Freshly prepared solutions in pentane gave spectra qualitatively similar to those of THF solutions, but decomposed over a few hours at room temperature, whereas the

THF solutions appeared stable. The solid spectra are appreciably more complex than those in solution, which is consistent with the expected extensive chlorine-bridging in the solid state. Although the THF solutions probably contain monomeric species, it is possible to draw few firm conclusions about their symmetry, as it is not clear whether or not the solvent will coordinate to the selenium atom. The most that can be said is that the relatively large number

TABLE 5

Vibrational Spectra of CF_3SeCF_3

Raman (cm^{-1})		Infrared (cm^{-1})		Assignment
		2330	w	$\nu_1 + \nu_9$
		2300	w	$2\nu_9$
		2240	w	$\nu_1 + \nu_2$
		2205	w	$\nu_2 + \nu_9$
		2040	vw	
		1890	w	$\nu_3 + \nu_9$
		1815	w	$\nu_2 + \nu_3$
		1710	w,br	$\nu_1 + \nu_4$
		1400	w	$\nu_2 + \nu_5$
		1275	m,sh	$\nu_3 + \nu_4$
		1195	vs	ν_1
1131	dp,vw,br	1160	s	ν_9
1057	p,w,br	1070	vs	ν_2 and ν_{10}
750	p,s	750	s	ν_3 and ν_{11}
		700	w	$\nu_5 + \nu_{13}$
545	w,sh			ν_4
536	dp,w	538	w	ν_{12}
364	p,m	362	m	ν_5
339	dp,m	345	w,sh	ν_{13}
280	p,s			ν_6
268	vw,br			
259	w,br			ν_{13}
112	dp,m,br			ν_7

ν_8 and ν_{15} not observed

of bands in the solution spectra below 400 cm^{-1}, where the Se-Cl stretching vibrations are expected, appears to preclude any structure with symmetry higher than C_s, particularly since at least four of the bands are polarized. However, if more than one species is present in solution, even this conclusion may be invalid.

(e) CF_3SeCF_3

The observed vibrational spectra of CF_3SeCF_3 are to be found in Table 5. A recent electron diffraction study[2] indicated that the probable molecular symmetry is C_{2v}. There are thus twenty-one normal modes, more than the number of bands observed which can plausibly be assigned as fundamental vibrations, and a rigorous assignment cannot be given.

Coupling between the two CF_3- groups leads to, for example, four modes which are basically asymmetric C-F stretches, of A_1, A_2, B_1 and B_2 symmetry. If, however, the coupling is small, some or all of these may be of very similar frequency. The simplified classification used here is based on C_2 symmetry, counting only one *A* and *B* combination of each of the six modes anticipated for a CF_3Se- group with local C_{3v} symmetry. The vibrations are described as

ν_1	$C-F_3$ asymmetric stretch	ν_9	$C-F_3$ asymmetric stretch
ν_2	$C-F_3$ symmetric stretch	ν_{10}	$C-F_3$ symmetric stretch
ν_3	CF_3 symmetric deformation	ν_{11}	CF_3 symmetric deformation
ν_4	CF_3 asymmetric deformation	ν_{12}	CF_3 asymmetric deformation
ν_5	C-Se stretch	ν_{13}	C-Se stretch
ν_6	CF_3 rock	ν_{14}	CF_3 rock
ν_7	C-Se-C bend	ν_{15}	CF_3 torsion
ν_8	CF_3 torsion		

$\nu_1 - \nu_8$ are *A* modes and Raman-polarized, while $\nu_9 - \nu_{15}$ are depolarized *B* modes. All are infrared active. The assignment follows largely from the work on CF_3SeH given earlier. In the C-F stretching region, the agreement between the infrared and Raman spectra is poor; while this is probably at least in part due to phase shifts, it is also possible that the full $\underline{C}_{2v}$ classification would be appropriate here, since the $\underline{A}_2$ combinations are allowed in the Raman effect, but not in the infrared. The $\underline{A}$ C-Se stretching occurs at higher frequency than the $\underline{B}$ mode. Such behaviour is relatively uncommon, but is also found in gaseous $SeCl_2$.[8] The intense $\underline{A}$ combination ν_6 of the CF_3 rocking mode is also observed in $(CF_3)_2PH$ and $(CF_3)_2AsH$,[5] as well as in $(CF_3)_2S$.[15] It is possible that the very weak Raman band at 268 cm^{-1} is a further rocking mode, but it could also be due to a combination involving the torsional modes ν_8 and ν_{15}, which were not observed directly. The lowest-frequency band in the Raman spectrum is assigned to the skeletal deformation ν_7. As for the other CF_3Se- derivatives discussed above, it appears depolarized, although is predicted to be polarized. The equivalent vibration in $(CF_3)_2S$, at 130 cm^{-1}, was observed to be polarized.[15]

(f) $\underline{CF_3SeSeCF_3}$

The observed vibrational spectra of $(CF_3Se)_2$ are presented in Table 6. The probable molecular symmetry, indicated by a recent electron diffraction study,[2] is $\underline{C}_2$, giving 24 normal modes, 13 $\underline{A}$ + 11 $\underline{B}$. Coupling between the two CF_3 groups gives rise, for example, to six C-F stretching modes 3 $\underline{A}$ and 3 $\underline{B}$. As for $(CF_3)_2Se$ above, it was found necessary to use a simplified classification, since it appears that the coupling is too small for all the fundamental vibrations to be resolved under the conditions used. The assignment adopted takes only one $\underline{A}$ and one $\underline{B}$ combination of each of the six modes expected for a CF_3Se- group of local $\underline{C}_{3v}$ symmetry, to which are added modes arising from motions of the CSeSeC skeleton.

TABLE 6

Vibrational Spectra of $CF_3SeSeCF_3$

Raman (cm^{-1})		Infrared (cm^{-1})		Assignment
		2250	w	$\nu_1 + \nu_{12}$
		2180	vw	$\nu_2 + \nu_{12}$
		1820	w	$\nu_3 + \nu_{12}$
		1780	vw	
		1270	m	$\nu_3 + \nu_4$
		1190	m,sh	
1170	dp,vw,br	1175	vs	ν_1
		1145	m,sh	ν_{11}
1105	p,w	1118	s	ν_2
		1090	s	ν_{12}
1072	vw,br	1070	s	$\nu_3 + \nu_{15}$
		1030	w	$\nu_1 + \nu_{16}$
		790	w	
740	p,s	740	m	ν_3 and ν_{13}
540	dp,w	535	mw	ν_4 and ν_{14}
339	p,ms			ν_5
332	m	330	w	ν_{15}
322	m			ν_6
288	dp,mw			ν_{16}
245	p,vs			ν_7
165	w			? $\nu_8 + \nu_{10}$ or ν_{18}
102	dp,m,br			ν_8 and ν_{17}
84	vw			ν_9

The vibrations may be described as:

$\nu_1 - \nu_6$	as $\nu_1 - \nu_6$ for $(CF_3)_2Se$ above
ν_7	Se–Se stretch
ν_8	Se–Se–C bend
ν_9	C–Se–Se–C torsion
ν_{10}–	CF_3 torsion

$\nu_{11} - \nu_{16}$ as $\nu_9 - \nu_{14}$ for $(CF_3)_2Se$ above

ν_{17} Se-Se-C bend

ν_{18} CF_3 torsion

Modes $\nu_1 - \nu_{10}$ are A species, and are expected to be Raman-polarized while the B vibrations are depolarized. All are infrared active.

Most of the assignment follows from that for CF_3SeH above. Perhaps the most interesting vibration frequency is that due to the Se-Se stretching motion, which is assigned to the strongest Raman band at 245 cm^{-1}. The values in Se_2Me_2, Se_2Cl_2 and Se_2Br_2 lie within the range 286 - 292 cm^{-1}.[9,10,16] A recent study of $(CF_3S)_2$ [15] assigned the S-S stretch to a medium intensity Raman band at 536 cm^{-1}, at somewhat higher frequency than the corresponding vibration in $(CH_3S)_2$, assigned to a very strong Raman band at 509 cm^{-1}.[16] It appears, then, that the assignment proposed here is inconsistent with that published for $(CF_3S)_2$.[15] It has been argued[16] that the occurence of the Se-Se stretching vibration within such a small range of frequencies in the molecules Se_2Me_2, Se_2Cl_2 and Se_2Br_2 is perhaps to be expected, as the skeletal bond angles are presumably near 90°, limiting coupling between the Se-X and Se-Se stretching motions. In the present case, however, there are vibrations of the CF_3 group which are of similar frequency to the Se-Se stretch, and coupling between these modes is not restricted by the geometry. It is thus plausible that the Se-Se stretching frequency in $(CF_3Se)_2$ should be lower than in $(CH_3Se)_2$. If this assignment is correct, it seems that in $(CF_3S)_2$ the S-S stretching frequency should be assigned to the strong Raman band at 452 cm^{-1}, rather than to the medium band at 536 cm^{-1}.

There is some ambiguity in the assignment of the B C-Se stretch and the A CF_3 rocking combination, since the overlapping of the bands prevents the measurement of their depolarization ratios. It is clear however, that the symmetric C-Se stretch is at higher frequency than the antisymmetric combination. This pattern is also found in Se_2Cl_2,

Se_2Br_2 [9,10] and Se_2Me_2.[16] The medium Raman band at 102 cm^{-1} is assigned as the A and B Se-Se-C bending combinations, the weak band at 84 cm^{-1} to the C-Se-Se-C torsion, leaving the weak band at 165 cm^{-1} possibly to a combination of the Se-Se-C bending motions and the CF_3 torsional modes. The resulting frequency of about 60 cm^{-1} for a CF_3 torsional motion seems reasonable.[12] Although the 165 cm^{-1} band could be assigned as an Se-Se-C bending mode, the resulting frequency separation between the A and B combinations of 63 cm^{-1} would be unappealingly large in view of the differences of 15, 11 and 17 cm^{-1} found for Se_2Cl_2, Se_2Br_2 and Se_2Me_2, respectively.[9,10,16] The study of $(CF_3S)_2$ [15] found only one Raman band to which the two bending modes were assigned.

Although this assignment appears reasonably satisfactory, one must remember that in a molecule of such low symmetry as $(CF_3Se)_2$, the thirteen A normal modes will be extensively mixed, and perhaps a detailed assignment of observed peaks to such shorthand descriptions as "Se-Se stretching motion" is not really justified without the results of a full normal coordinate analysis.

2. N.M.R. Spectra

A wide range of CF_3Se- derivatives have been studied during the course of this work. The chemical shifts observed, recorded under comparable conditions, are presented in Table 7. In general, the more electronegative is the group attached to selenium, the more the CF_3 resonance is shifted to higher field. This trend is the opposite of that expected on elementary electron-withdrawing theory. "Apparently anomalous" trends in ^{19}F chemical shifts have frequently been observed,[17] and it appears that there is no simple, generally applicable theory to account for the shifts observed.

TABLE 7

Fluorine Chemical Shifts in CF_3Se- Derivatives

	shift[a]
$CF_3SeTlMe_2$*	12.6
$Hg(SeCF_3)_2$	15.53
$CF_3SeSiMe_3$*	22.79
CF_3SePF_2*	23.48
CF_3SeH	25.30
CF_3SeCN	31.42
CF_3SeCF_3	31.98
$CF_3SeSeCF_3$	38.10
CF_3SeBr	39.56
CF_3SeCl	41.99
CF_3SeCl_3	51.02

[a] Values in ppm upfield from CCl_3F resonance

* See following paper for details of preparation and characterisation

TABLE 8

$^2J(^{77}Se\ ..\ F)$ Coupling Constants in CF_3Se- Derivatives

	J (Hz)
$CF_3SeSeCF_3$	6.5
CF_3SeCF_3	11.2
CF_3SeH	12
CF_3SePF_2	18.6
CF_3SeCl	35
$Hg(SeCF_3)_2$	39.8
CF_3SeCN	54

Selenium contains about 7.5% ^{77}Se in natural abundance, for which isotope I = ½. Selenium-fluorine two bond coupling constants are given in Table 8 for those compounds in which coupling has been observed. No clear trends are discernible in the values given. It must be remembered that the coupling constants are not necessarily of the same sign. In a few molecules, ^{13}C satellites were observed in the ^{19}F spectra. Values of the directly-bonded ^{13}C-F coupling constants in Hz are: $Hg(SeCF_3)_2$, 329.6; CF_3SeH, 331; CF_3SeCF_3, 332.6; $CF_3SeSeCF_3$, 337. In CF_3SeCF_3, the ^{13}C satellites in the fluorine spectra appear as quartets, since the two sets of three fluorines are not equivalent in those molecules with one ^{13}C atom and one ^{12}C atom. The four-bond F ... F coupling constant is 8.7 Hz. In $(CF_3Se)_2$, the analogous five-bond F ... F coupling constant is 3.1 Hz. The H ... F coupling constant in CF_3SeH is 7.5 Hz.

No coupling from fluorine to mercury was seen in the room temperature ^{19}F spectra of $Hg(SeCF_3)_2$. Suspecting that this might be due to exchange of $SeCF_3$ groups between different mercury atoms, a series of spectra were recorded at temperatures down to -80°C, using $(CD_3)_2CO$ as solvent. At that temperature, all lines (including that of CCl_3F) were beginning to broaden slightly, presumably as a result of the increased viscosity. No coupling to mercury was detected. The chemical shift decreased by 0.41 ppm, while the Se ... F coupling constant increased to 43.6 Hz.

Investigation by n.m.r. spectroscopy of the behaviour of a mixture of bromine and $(CF_3Se)_2$, showed that, contrary to the original report,[1] reaction occurs readily at the slightly elevated temperature of an n.m.r. instrument to give CF_3SeBr. The reaction was found to be incomplete, with some $(CF_3Se)_2$ remaining even in the presence of excess bromine. The volatile products of the reaction between bromine and $Hg(SeCF_3)_2$ were also shown to contain some $(CF_3Se)_2$, indicating that an equilibrium is set up:

$$(CF_3Se)_2 + Br_2 \rightleftharpoons 2CF_3SeBr$$

Attempts to measure the equilibrium constant were not successful. Small differences in ratios of components led to large differences in the apparent value of the equilibrium constant. It is large, of the order of 100. This equilibrium was not detected by vibrational spectroscopy, a technique much less suitable than n.m.r. spectroscopy in the present case, as by n.m.r. the lines due to the various species are easily resolved, whereas in the vibrational spectra they overlap extensively.

By examing the behaviour of a mixture of chlorine and bromine on $(CF_3Se)_2$, it was shown that the CF_3Se- group has greater affinity for Cl than for Br. A 1:1:1 mixture of these three reagents resulted in a $CF_3SeCl:CF_3SeBr$ ratio of about 5:1, with no residual $(CF_3Se)_2$ detectable. The two species were shown to be exchanging halogens, since their n.m.r. signals were appreciably broadened towards each other. The signal due to CF_3SeCl_3 is also broadened by the addition of excess chlorine. No extra signals due to species such as CF_3SeBr_3, $CF_3SeClBr_2$ or CF_3SeCl_2Br could be detected in these studies.

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