

## A Sapphire Cell for High-temperature Raman Studies of Reactive Gases. The Vibrational Spectra of SeF<sub>4</sub>, SeOF<sub>2</sub>, TiF<sub>4</sub>, and SbF<sub>3</sub>

By Lesley E. Alexander and I. R. Beattie,\* Department of Chemistry, The University, Southampton SO9 5NH

The vibrational spectra of TiF<sub>4</sub> (Raman: solid, gas), SbF<sub>3</sub> (Raman: solid, gas, solution in methanol; infrared: solid), SeOF<sub>2</sub> (Raman: solid, liquid, gas), SeF<sub>4</sub> (Raman: solid (two forms), liquid, gas; i.r.: gas) are reported. The use of vibrational spectroscopy to study polymerisation in condensed phases is discussed with particular reference to ClF<sub>3</sub> and the title compounds.

THE study of the Raman spectra of gases at temperatures up to 1000 °C can be considered to be routine for samples which do not attack silica. However, with many compounds, notably fluorides, rapid attack of borosilicate and silica cells occurs as the temperature is raised above ambient. We approached the problem of cell corrosion in two ways: (a) by the design of metal cells with sapphire windows; (b) by the design of an all-sapphire cell. In both cases the problem of gasket materials arises. The only material known to us which is sufficiently soft to form a vacuum seal and sufficiently inert to withstand prolonged contact with fluorides at reasonably high temperatures is polytetrafluoroethylene. However, difficulties arise when this material is heated above 400 °C.

The metal cell with sapphire windows used a gold O-ring as the high temperature seal. By use of the thick sapphire window as essentially an insulating material of the furnace, it is possible to make a lower temperature (water cooled) high-vacuum O-ring seal in polytetrafluoroethylene on the outside of the window. In the case of the all-sapphire cell (which was used for the experiments described here) it was possible to use a polytetrafluoroethylene seal up to 400 °C providing that (a) the sealing faces were optically polished and (b) a very thin (ca. 0.002 in) polytetrafluoroethylene seal was used, with the two sealing surfaces in compression.

*Titanium Tetrafluoride.*—The physical properties of titanium tetrafluoride show that it is polymeric in the

titanium is probable. Table 1 shows the Raman spectrum of solid titanium tetrafluoride and also as a gas at 300 °C.

There are no molecular weight data available for gaseous titanium tetrafluoride but the close similarity between the vibrational spectra of germanium tetrafluoride<sup>1</sup> and titanium tetrafluoride in terms of position, number of bands, and polarisation characteristics strongly suggests the presence of monomeric tetrahedral units. The weakness of  $\nu_3$  is, however, surprising and we note that under conditions where this band was observed a weaker band at 1017 cm<sup>-1</sup> also showed the presence of a small amount of a Ti-terminal oxygen species.

The totally symmetric mode of gaseous tin tetrafluoride is, by analogy with germanium tetrafluoride, expected to be just below 700 cm<sup>-1</sup>. This is ca. 80 cm<sup>-1</sup> higher than the totally symmetric stretching mode of the (polymeric) solid,<sup>2</sup> at 621 cm<sup>-1</sup>. By contrast, for titanium tetrafluoride the frequency change from gas to solid for the most intense Raman band in the 'titanium-fluorine stretching region' is an increase of ca. 100 cm<sup>-1</sup>. It is probable that tin tetrafluoride and titanium tetrafluoride have different structures in the solid state. Tin tetrafluoride is polymeric with *trans*-terminal fluorines,<sup>3</sup> while VOF<sub>3</sub> and presumably VF<sub>4</sub> have *cis*-terminal oxygen and fluorine or fluorines respectively.<sup>4</sup> For VOF<sub>3</sub> the frequency change from gas<sup>5</sup> to solid<sup>6</sup> is an increase of 20 cm<sup>-1</sup>.

*Antimony Trifluoride.*—The solid-state structure of antimony trifluoride can be described<sup>7</sup> as based on a basic C<sub>3v</sub> SbF<sub>3</sub> unit with mean Sb-F distances of 1.92 Å, together with additional fluorines at an average Sb-F distance of 2.61 Å and completing the distorted octahedron about the central antimony. There are two molecules in the unit cell which is not centrosymmetric. Our solid-state spectra (Table 2) agree with those given by Downs and Adams.<sup>8</sup> Similarly, our gas-phase Raman spectra taken at 330 °C agree satisfactorily with the earlier i.r. matrix isolation studies.<sup>8</sup> The bands are readily assigned on the basis of the expected C<sub>3v</sub> monomer. Table 2 also reports data for a solution of antimony trifluoride in methanol, although the assignments in this

TABLE 1  
Vibrational spectra of TiF<sub>4</sub> and GeF<sub>4</sub>

TiF <sub>4</sub> (solid) Raman	TiF <sub>4</sub> (gas) Raman	GeF <sub>4</sub> (gas) <sup>a</sup>	Assignments (gas phase)
817s	793vww	800	$\nu_3$
770m,sh	712vs,p	738	$\nu_1$
494w			
466w			
367w			
236w	209s,br	260	$\nu_4$
208w	185s	205	$\nu_2$
138w			

<sup>a</sup> From ref. 1.

solid state. Although no detailed X-ray structural study is available, a structure based on six-co-ordinated

<sup>1</sup> A. D. Caunt, L. N. Short, and L. A. Woodward, *Trans. Faraday Soc.*, 1952, **48**, 873; see also (for SiF<sub>4</sub>) R. J. H. Clark and D. M. Rippon, *Chem. Comm.*, 1971, 1295.

<sup>2</sup> I. R. Beattie, N. Cheetham, T. R. Gilson, K. M. S. Livingston, and D. J. Reynolds, *J. Chem. Soc. (A)*, 1971, 1910.

<sup>3</sup> W. Dähne and R. Hoppe, *Naturwiss.*, 1962, **49**, 254.

<sup>4</sup> A. J. Edwards and P. Taylor, 6th International Symposium on Fluorine Chemistry, Durham, 1971.

<sup>5</sup> H. Selig and H. H. Claassen, *J. Chem. Phys.*, 1966, **44**, 1404.

<sup>6</sup> I. R. Beattie, K. M. S. Livingston, D. J. Reynolds, and G. A. S. Ozin, *J. Chem. Soc. (A)*, 1970, 1210.

<sup>7</sup> A. J. Edwards, *J. Chem. Soc. (A)*, 1970, 2751.

<sup>8</sup> A. J. Downs and C. J. Adams, *J. Chem. Soc. (A)*, 1971, 1534.

case rely on the absence of reaction and can only be taken as tentative.

TABLE 2  
Vibrational spectra of  $\text{SbF}_3$

Solid		Matrix isolation <sup>a</sup> i.r.	Gas R.	Solution in MeOH R.
I.r.	R.			
725m				
600m	503vs	645m	666s,p	593s,p
473vs	462s	624s	634m	530m
271m	284mw			
248m	257w	259m	250m,p	270w
226m	233vw			235w
215m	220w			
	173mw			
	153mw			
	125mw			
	98mw			

<sup>a</sup> Ref. 8.

*Selenium Oxide Difluoride.*—The physical properties of this compound suggest that it is essentially monomeric in the liquid, although some degree of intermolecular

TABLE 3  
Raman spectra of  $\text{SeOF}_2$

Solid	Liquid <sup>a</sup>	Liquid (this work)	Gas	Assignments	
979w,sh					
968w,sh					
956vs	1012vs,p	1007vs,p	1049vs,p	$A'$	$\nu_1$
698s	664s,p	658vs,p	667vs,p <sup>b</sup>	$A'$	$\nu_3$
658w	605s	603s	637m,br	$A''$	$\nu_5$
648w					
622ms					
610ms					
400w					
388w	377m,p	375m	362m,p	$A'$	$\nu_3$
380mw					
304m	308m	309ms	282m,br	$A''$	$\nu_5$
293w					
135mw	278mw,p	283m	253vw,p?	$A'$	$\nu_4$
110ms					
98w					
77w					
50s					

<sup>a</sup> Ref. 10. <sup>b</sup> The poor quality gas-phase i.r. spectrum showed one band at  $670\text{ cm}^{-1}$ .

interaction in condensed phases would not be unexpected. Figure 1 shows the Raman spectra of solid, liquid, and gaseous ( $120^\circ\text{C}$ ) selenium oxide difluoride. Although there are frequency shifts and some major relative intensity effects, the differences are not sufficiently great to assume the presence of discrete polymeric species in the liquid. Gaseous  $\text{SeOF}_2$  is known to be monomeric<sup>9</sup> and assignments appear to be unambiguous, except for the  $253\text{ cm}^{-1}$  band which is questionable (Table 3). For the liquid the agreement with the work of Rolfe and Woodward<sup>10</sup> is acceptable.

*Selenium Tetrafluoride.*—Selenium tetrafluoride is in an interesting portion of the Periodic Table from the point of view of polymerisation *via* fluorine bridging.

<sup>9</sup> E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *J. Chem. Soc.*, 1952, 1231.

<sup>10</sup> J. A. Rolfe and L. A. Woodward, *Trans. Faraday Soc.*, 1955, 51, 779.

Figure 2 summarises the situation for the non-transition elements. It raises some problems about techniques for studying polymerisation and in particular it is perhaps relevant to enquire what is meant by the physicist

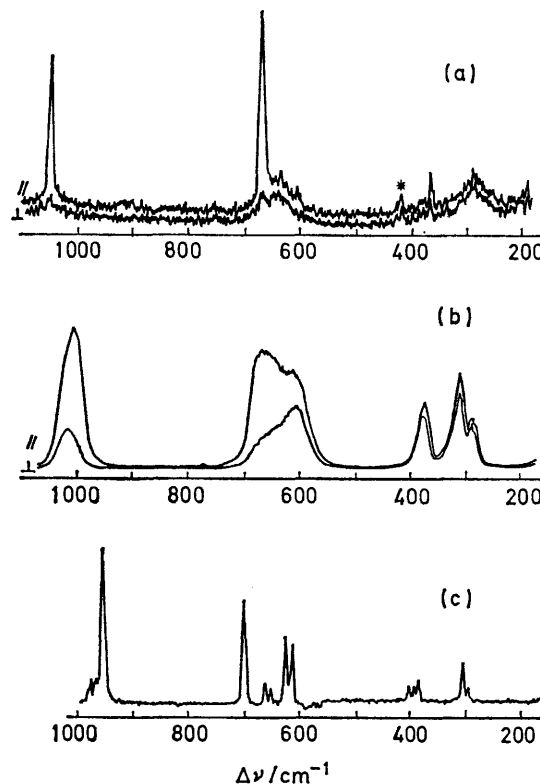


FIGURE 1 The Raman spectra of selenium oxide difluoride; (a), gas; (b), liquid; (c), solid; \* sapphire

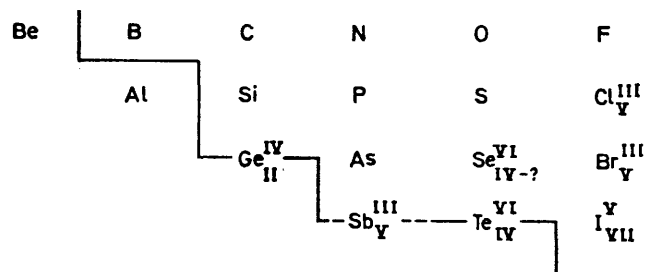


FIGURE 2 Approximate representation of polymerisation (*via* fluorine bridging) of non-transition element fluorides. Compounds shown below the line are essentially polymeric in the solid state

and by the chemist with respect to terms such as 'dimerisation'. We shall consider initially one case in some detail, that of chlorine trifluoride, which has recently been studied by matrix isolation techniques<sup>11</sup> by use of i.r. spectroscopy. Chlorine trifluoride is a rigorously planar molecule in the solid state by X-ray diffraction techniques.<sup>12</sup> The 'axial' Cl-F bond

<sup>11</sup> R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, 1971, 54, 344.

<sup>12</sup> R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, 1953, 21, 602.

distance is 1.72 Å, the 'equatorial' distance 1.62 Å, and the bond angle 87°. The next nearest Cl-F distance is 3.06 Å. Microwave spectroscopy gives closely similar results for the gaseous species: <sup>13</sup> axial Cl-F, 1.698 Å;

the concentration of dimers was *ca.* 4%. However, work by Adams and his co-workers <sup>15</sup> suggested that the gas was essentially monomeric at -40 °C. Selig *et al.* <sup>16</sup> on the basis of Raman studies, stated 'We

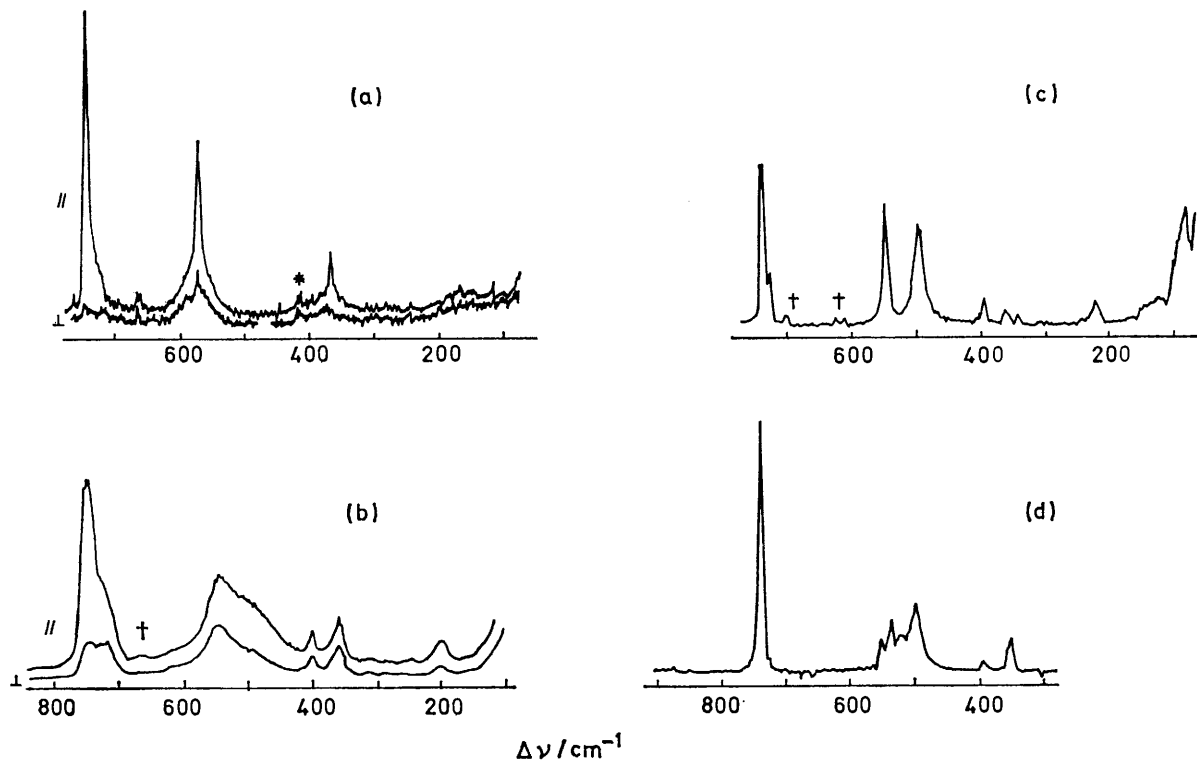


FIGURE 3 The Raman spectra of selenium tetrafluoride; (a), gas; (b), liquid; (c), solid; (d)? crystalline solid, \* sapphire, † SeOF<sub>2</sub>

TABLE 4  
Vibrational spectra of SeF<sub>4</sub>

Raman				Gas i.r.	
Solid(I) <sup>a</sup>	Solid(II)	Liquid <sup>a</sup>	Gas	This work	Ref. 24
742vs				744s	745vs, PQR
736vs	742vs	748vs, p	749vs, p	674w, PQR <sup>b</sup>	736vs, br
728w, sh	728vw, sh	720w, sh	724w, sh	634vs, QQ?	622vs, PQR
			590vw, sh		
			574s, p		
548s	552m	542s, p	559vw, sh		
496s	540m				
	521m				
	500ms	484s, p			
395m	391w	400w			
			374w		
361w	350m	357	366m, p	367m	
341w					
220mw		200w	162w, p?		
139w					
119w	98w				
80m	80w				

<sup>a</sup> Weak bands due to SeOF<sub>2</sub> impurity omitted. <sup>b</sup> SeOF<sub>2</sub>?

'equatorial' Cl-F, 1.598 Å; angle 87° 29'. To most chemists this compound would be considered to be monomeric in the solid state. Earlier molecular weight studies <sup>14</sup> on the gas suggested that at the b.p. (11.75 °C)

<sup>13</sup> D. F. Smith, *J. Chem. Phys.*, 1953, **21**, 609.

<sup>14</sup> H. Schmitz and H. J. Schumacher, *Z. Naturforsch.*, 1947, **2a**, 363.

believe . . . that the degree of dimerisation in the gas, if any, must be much lower than the 4% indicated by early data.'




























<sup>15</sup> R. M. Adams, R. B. Bernstein, and J. J. Katz, *J. Chem. Phys.*, 1954, **22**, 13.

<sup>16</sup> H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 1970, **52**, 3517.

The i.r. spectrum of the gas<sup>16</sup> and of the solid<sup>11</sup> show differences between the two spectra, notably in the region of  $\nu_4$ : gas-phase spectrum 702  $\text{cm}^{-1}$ ; solid-state spectrum 610  $\text{cm}^{-1}$  very broad. In matrices<sup>11</sup> bands in the 666–626  $\text{cm}^{-1}$  region have been attributed to the

$\text{ClF}_3$  molecule interacts weakly with an adjacent  $\text{ClF}_3$  molecule in preference to a weak interaction with the surrounding matrix. Thus vibrational spectroscopy, although useful for studying polymerisations, must be used with caution. Quite large changes in frequency,

TABLE 5  
Correlation of the fundamental modes of vibration of  $\text{SeF}_4$  and  $\text{SF}_4$  with those of  $\text{AsF}_5$  and  $\text{BrF}_3$  †

BrF <sub>3</sub>		AsF <sub>5</sub>		SeF <sub>4</sub>		SF <sub>4</sub>
Mode	Assignment/cm <sup>-1</sup>	Mode	Assignment/cm <sup>-1</sup>	Mode	Assignment/cm <sup>-1</sup>	
 a <sub>1</sub>	675	 a' <sub>1</sub>	734	 a <sub>1</sub>	749	892
		 e' <sub>a</sub>	811			
b <sub>2</sub> (translation)		 e' <sub>b</sub>	811	 b <sub>2</sub>	736*	867
 b <sub>1</sub>	612	 a'' <sub>2</sub>	784	 b <sub>1</sub>	622*	730
 a <sub>1</sub>	552	 a' <sub>1</sub>	644	 a <sub>1</sub>	574	559
 b <sub>1</sub>	350	 a'' <sub>2</sub>	400	 b <sub>1</sub>	—	532
		 e'' <sub>a</sub>	386			
a <sub>2</sub> (rotation)		 e'' <sub>b</sub>	386	 a <sub>2</sub>	—	414
a <sub>1</sub> (translation)		 e' <sub>a</sub>	372	 a <sub>1</sub>	365	464
b <sub>2</sub> (rotation)		 e' <sub>b</sub>	372	b <sub>2</sub> (rotation)		
 a <sub>1</sub>	233	 e' <sub>a</sub>	130	 a <sub>1</sub>	162	226
 b <sub>2</sub>	242	 e' <sub>b</sub>	130	 b <sub>2</sub>	—	353

\* Value taken from ref. 24. † Symmetry co-ordinates are used to describe approximately the fundamental modes. Coupling will be serious, notably for the two e' modes of AsF<sub>5</sub>.

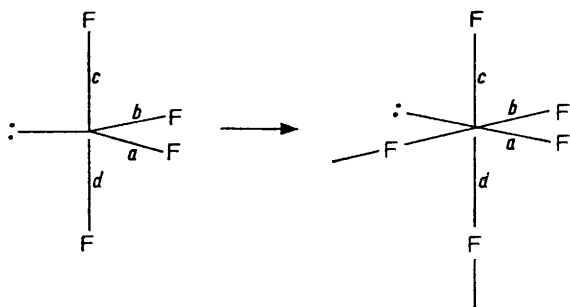
formation of dimers and higher polymers. In view of the known structure of gaseous and solid  $\text{ClF}_3$ , together with the gas-phase molecular weight data, it is clear that these bands are not due to the dimers and higher polymers with which chemists normally deal. The spectral changes may be an indication that an isolated

band contour, and relative intensity may occur owing to phenomena which are linked with weak association in condensed phases, rather than with the formation of chemically important polymeric species.

It is impossible to draw a sharp distinction between the two extremes of monomer and polymer. However,

species such as  $\text{IF}_5$ ,<sup>17</sup>  $\text{ClF}_3$ , and  $\text{BrF}_3$ <sup>11</sup> are best regarded as associated liquids. Species such as  $\text{BeF}_2$ ,<sup>18</sup>  $\text{GeF}_2$ ,<sup>19</sup> and  $\text{TeF}_4$ <sup>20</sup> are unambiguously polymeric (in the solid state).

Table 4 and Figure 3 report the Raman spectra of selenium tetrafluoride as a gas (known to be monomeric<sup>9</sup>), as a liquid, and as a solid (apparently two forms), and the i.r. spectrum of the gas. Table 5 compares the gas-phase results with those for the related molecules  $\text{AsF}_5$ ,<sup>21</sup>  $\text{BrF}_3$ ,<sup>16</sup> and  $\text{SF}_4$ <sup>11</sup> (see also ref. 22). The assignments require little discussion as they follow



from the polarisation data, activity, and position in terms of the related molecules tabulated. The agreement of our Raman work on the liquid with that of Rolfe, Woodward, and Long<sup>23</sup> is acceptable. It is clear from the successive changes gas  $\rightarrow$  liquid  $\rightarrow$  solid  $\rightarrow$  ? crystalline solid that for selenium tetrafluoride there are considerable interactions present in the liquid and in the solid. Similar suggestions have been made from i.r. studies by use of matrix isolation techniques.<sup>24</sup>

Consideration of the molecular shape of  $\text{SeF}_4$  indicates that a loose polymerisation towards the  $\text{TeF}_4$  structure results in a perturbed  $C_{2v}$  molecule. In Sidgwick and Powell terms it is necessary to move the equatorial lone pair through an angle of  $30^\circ$ , while closing the  $\text{SeF}_2$  equatorial angle by  $30^\circ$ . This procedure would be expected to lead to a strengthening of bonds  $a$  and  $c$  and a weakening of bonds  $b$  and  $d$ . The values found<sup>20</sup> in the crystal-structure determination of  $\text{TeF}_4$  are:  $a = 1.80$ ,  $b = 1.87$ ,  $c = 1.92$ ,  $d = 2.08$ ,  $e = 2.26$  Å. For gaseous  $\text{SeF}_4$  the values are<sup>25</sup>  $a = b = 1.682$ ,  $c = d = 1.771$  Å with angles of  $100.55$  and  $169.20^\circ$ . It is clear that such interactions can lead to: (a) a perturbed  $C_{2v}$   $\text{SeF}_4$  molecule; (b) a perturbed  $\text{SeF}_3^+$  pyramidal ion; or (c) a fluorine-bridged polymer containing an effectively square pyramidal distribution about the selenium.

<sup>17</sup> See, e.g., L. E. Alexander and I. R. Beattie, *J. Chem. Soc. (A)*, 1971, 3091.

<sup>18</sup> A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, 1962.

<sup>19</sup> J. Trotter, M. Akhtar, and N. Bartlett, *J. Chem. Soc. (A)*, 1966, 30.

<sup>20</sup> A. J. Edwards and F. I. Hewaidy, *J. Chem. Soc. (A)*, 1968, 2977.

<sup>21</sup> L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, 1971, **55**, 5063.

<sup>22</sup> K. O. Christe and W. Sawodny, *J. Chem. Phys.*, 1970, **52**, 6320; I. W. Levin, *ibid.*, 1971, **55**, 5393, and references therein.

Even with crystallographic data the point of view adopted may be dependent upon the observer. Certainly vibrational spectroscopy is not the technique to make such distinctions in the solid state or in the liquid. We note that the  $^{19}\text{F}$  n.m.r. spectrum of  $\text{SeF}_4$  at the m.p. ( $-9^\circ\text{C}$ ) shows only one resonance<sup>26</sup> for the liquid so that this gives no additional information regarding the nature of the association.

#### EXPERIMENTAL

**Preparations.**—Titanium tetrafluoride was prepared by direct fluorination of titanium metal, followed by vacuum sublimation.<sup>27</sup> Antimony trifluoride was a commercial sample purified by repeated vacuum sublimation. Selenium tetrafluoride was prepared by slow fluorination of a sublimed film of selenium in a silica vessel at  $0^\circ\text{C}$ .<sup>9</sup> (Great care is necessary to avoid the formation of the oxide difluoride as an impurity.) The product was distilled in a glass vacuum line that had been thoroughly outgassed. The ampoules were stored at liquid-nitrogen temperature. Selenium oxide difluoride was prepared by the reaction between selenium dioxide and selenium tetrafluoride, followed by distillation.<sup>28</sup>

**High-temperature Raman Cell.**—The cell is shown in Figure 4. Loading is carried out in a glove-box flushed with dry air, nitrogen, or argon. The Teflon washer is placed in position and the bolts tightened to press the cap on to the main body. If nitrogen or air is used in the box this has the advantage that the spectrometer can be aligned by use of the rotational spectrum of nitrogen or air.

Because of the direction of growth of the original sapphire boule, the optic axis of the sapphire is at ca.  $15^\circ$  to the geometrical axis of the cell. It is thus essential to orientate

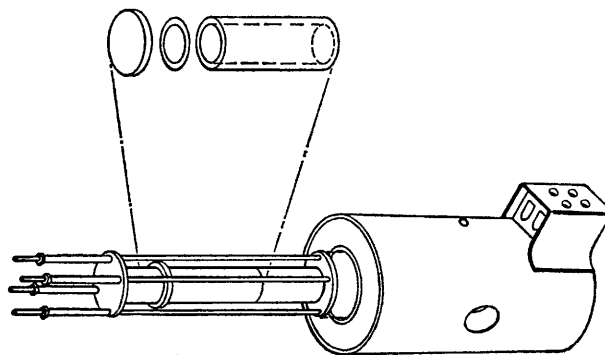


FIGURE 4 The sapphire cell and furnace assembly

the cell in such a position in the spectrometer that the incident laser beam is not depolarised. This is achieved by orienting the cell such that the optic axis and the tube axis lie in the same vertical plane. For collection of Raman

<sup>23</sup> J. A. Rolfe, L. A. Woodward, and D. A. Long, *Trans. Faraday Soc.*, 1953, **49**, 1388.

<sup>24</sup> E. E. Aynsley, R. E. Dodd, and R. Little, *Spectrochim. Acta*, 1962, **18**, 1005.

<sup>25</sup> L. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectroscopy*, 1968, **28**, 454.

<sup>26</sup> E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084.

<sup>27</sup> H. M. Haendler, S. F. Bartram, R. S. Becker, W. J. Bernard, and S. W. Bukata, *J. Amer. Chem. Soc.*, 1954, **76**, 2177.

<sup>28</sup> R. D. Peacock, *J. Chem. Soc.*, 1953, 3617.

light ideally the tube should be aligned at  $15^\circ$  to the horizontal. In practice this is inconvenient, so that depolarisation ratios are inaccurate in the absence of suitable calibration.

*Spectra.*—Raman spectra were all run with a Spex 1401 spectrometer and a Spectra Physics Model 140 or 165 argon laser. The i.r. spectrometer used was a Beckman IR11. Gas-phase i.r. spectra of selenium oxide fluoride and

selenium tetrafluoride were run in a silica cell with polypropylene windows. The spectra were of poor quality in both cases. The solid-state i.r. spectrum of antimony trifluoride was run in Nujol between caesium iodide plates.

We thank Dr. T. R. Gilson for discussion, Esso Petroleum for a maintenance grant, and the S.R.C. for support.

[2/489 Received, 2nd March, 1972]

---