Vibrational Spectra of Niobium and Tantalum Pentafluorides in the Gas Phase. The Vapour Density of Niobium Pentafluoride

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Molecular weight data obtained through mass spectrometry and vapour density measurements show that at lower temperatures gaseous niobium and tantalum pentafluorides contain polymers. The results suggest the presence of monomeric, dimeric, and trimeric species.

The Raman spectra of the gaseous pentafluorides as a function of temperature confirm that (reversible) dissociation occurs as the temperature is raised. The i.r. spectra of these two compounds in the gas phase at temperatures and pressures where there is extensive polymerisation are in agreement with the presence of octahedrally co-ordinated metal atoms with *cis*-fluorine bridges. The i.r. spectrum of molten niobium pentafluoride is closely related to that of the gas at lower temperatures and to that of the solid, which is known to be polymeric.

THE interpretation of the Raman spectra of the pentafluorides of niobium and tantalum in the liquid state and of the i.r. spectrum of gaseous niobium pentafluoride are in dispute. Chronologically Blanchard[1] interpreted the gas-phase i.r. spectrum on the basis of a D_{3h} monomer. Selig *et al.*[2] suggested on the basis of Raman observations that niobium and tantalum pentafluorides were monomeric in the melt. Beattie and his co-workers[3] disputed the interpretation of both previous groups of workers and in particular suggested that the spectroscopic data could be interpreted in terms of *cis*-fluorine-bridged polymers analogous to antimony pentafluoride.[4] More recently Ouellette, Ratcliffe, and Sharp,[5] on the basis of the similarity of the Raman spectra of molten molybdenum and tantalum pentafluorides, coupled with mass spectrometric studies[6] showing gaseous molybdenum pentafluoride to be monomeric, have suggested that molybdenum, niobium, and tantalum pentafluoride are monomeric in the melt.

Apart from these vibrational studies, electron-diffraction techniques have been reported to show the presence of polymeric species in gaseous niobium and tantalum pentafluorides.[7] More recently the ^{19}F n.m.r. spectrum of molten niobium pentafluoride has been interpreted as showing the presence of monomers.[8] However, we are not able to follow the reasoning behind this analysis if a rapid fluorine exchange process is operative, as seems highly likely. Clearly a reinvestigation of this system is desirable to clarify the polymerisation behaviour of the melt and gas. In Table 1 we record the apparent molecular weight of niobium pentafluoride for various temperatures and pressures. These results were obtained by what is essentially an instantaneous Victor Meyer technique designed to minimise corrosion of the apparatus. Less successful experiments were carried out in a Monel cell with a Monel bellows to transmit the pressure to a measuring device. Although mass spectrometric studies were also attempted these only served to establish the likely presence of primary monomer, dimer, and trimer.[9] No quantitative data were obtained about the relative amounts of each species in the gas phase. Thus although the vapour-density measurements unambiguously show the presence of polymers at lower temperatures and of mainly monomer at the highest temperature, the results are not sufficiently extensive or accurate to enable a detailed analysis to be carried out.

TABLE 1

Gas-phase molecular weight data for niobium pentafluoride †

Temp./°C	Wt. taken/g	p/mmHg	Apparent mol. wt.	Degree of polymerisation
246	0·2282	76	496	2·6
248	0·2340	87	453	2·4
263	0·0853	43	343	1·8
266	0·2970	124	419	2·2
271	0·076	92	346	1·8
330	0·1871	132	276	1·4
334	0·0768	72	209	1·1
405	0·2429	246	214	1·15

† Calculated for monomer 188.

Figures 1 and 2 show the Raman spectra of gaseous niobium and tantalum pentafluorides as a function of temperature. The spectra are taken from several experiments and include both heating and cooling cycles. Cell attack was avoided by the use of an all-sapphire cell with a Teflon gasket.[10] Some experiments were also carried out with a Monel metal cell[10] with sapphire windows incorporating both gold and Teflon O-rings. The results of these experiments demonstrate that these pentafluorides undergo reversible dissociation on heating and, taken in conjunction with the molecular weight measurements, show one strong Raman band for the monomeric pentafluorides in the stretching region.

If we assume that polymerisation occurs *via cis*-fluorine bridges of an 'octahedral' NbF_6 unit, then

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[1] S. Blanchard, *J. Chim. phys.*, 1965, **62**, 919.

[2] H. Selig, A. Reis, and E. L. Gasner, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2087.

[3] I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1969, 958.

[4] C. A. Hoffmann, B. E. Holder, and W. L. Jolly, *J. Phys. Chem.*, 1958, **62**, 364; E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.

[5] T. J. Ouellette, E. T. Ratcliffe, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1969, 2354.

[6] T. J. Ouellette, cited in ref. 5.

[7] G. V. Romanov and V. P. Spiridonov, *Vestnik Moskov. Univ.*, 1968, no. 5, 7—11; G. V. Romanov and V. P. Spiridonov, *Izvest. Sibersk. Otdel. Akad. Nauk S.S.S.R.*, *Ser. khim. Nauk*, 1968, no. 1, 126.

[8] L. Kolditz, U. Calov, and A-R. Grimmer, *Z. Chem.*, 1970, **10**, 35.

[9] B. Phillips and M. H. Rand, personal communication.

[10] L. E. Alexander and I. R. Beattie, to be published.

the spectroscopically important features are likely to be the vibrations of the C_{2v} MF_4 residue together with the fluorine bridge modes which are in practice only likely to be intense in the i.r. spectrum. By analogy with gaseous tellurium tetrachloride[11] we expect in the Raman spectrum two strong polarised bands, effectively the axial NbF_2 symmetric stretching mode and the equatorial NbF_2 symmetric stretching mode. In the i.r. effect we expect three stretching modes to be intense, the axial NbF_2 antisymmetric stretch and the equatorial NbF_2 symmetric and antisymmetric stretches. In addition to this at lower frequencies we expect broad bridge modes in the i.r. effect. An important feature is that for the stretching region the Raman spectrum of the polymer is likely to be independent of ring size.

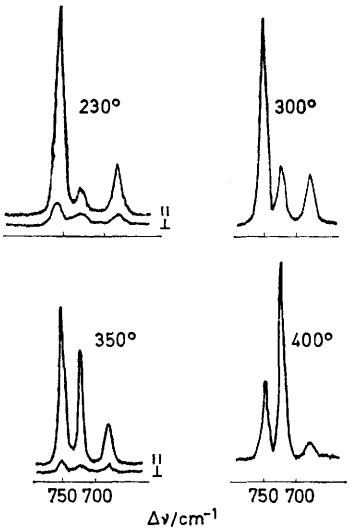

FIGURE 1 The Raman spectrum (in the 700 cm^{-1} region) of gaseous niobium pentafluoride as a function of temperature

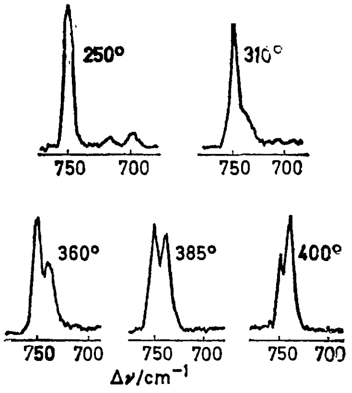

FIGURE 2 The Raman spectrum (in the 700 cm^{-1} region) of gaseous tantalum pentafluoride as a function of temperature

For the monomer, by analogy with AsF_5 for example,[12] we expect one strong polarised band in the stretching region in the Raman effect, inactive in the i.r. spectrum. Two intense bands are expected for the i.r. spectrum in the stretching region, one of these formally being Raman-active but only expected to be weak in the Raman spectrum. Although there is one other totally symmetric stretching mode for the monomer this band is usually weak in the Raman effect for related molecules and only very slightly polarised (essentially owing to out-of-phase coupling).

The Raman spectra of both the gaseous pentafluorides at low temperature show two polarised bands in agreement with the presence of a C_{2v} MF_4 residue. The characteristic changes of the spectra with temperature lead in each case to a dominant species (at temperatures of the order of 400°) which is monomeric and shows only one strong stretching frequency. Although it is clearly not possible to assign a symmetry to this molecule the results do not disagree with the presence of a trigonal bipyramidal species.[*]

I.r. gas-phase studies were also made on niobium and tantalum pentafluorides at temperatures just above the m.p. Silver chloride windows were used to reduce corrosion, but some attack occurred so that caution is necessary in interpreting the spectra. However, our results on niobium pentafluoride are closely similar to those of Blanchard.[1] Our interpretation is quite different. We attribute the three strong bands in the i.r. spectrum of gaseous niobium and tantalum pentafluorides to fundamental modes of vibration of the C_{2v} MF_4 residue. Our Raman results exclude the presence of appreciable quantities of monomer at the temperature of the i.r. experiment. Further, we attribute the broad bands in the region of 510 cm^{-1} to fluorine bridge modes (see Table 2).

In the i.r. spectrum of arsenic pentafluoride stretching modes occur at 811 and 787 cm^{-1}, the deformations occurring at 400 and 369 cm^{-1}. The frequency difference between the lowest stretch and highest deformation for arsenic pentafluoride is thus 387 cm^{-1}. For gaseous niobium and tantalum pentafluoride the difference between the supposed bridging mode and the lowest stretching mode is 179 and 168 cm^{-1} respectively. We feel this strongly supports our assignment of this mode not as a deformation but as a bridge mode of a polymeric species. The assignment also agrees with earlier work[3] on solid (tetrameric) niobium pentafluoride.

In Table 1 we also record the i.r. spectrum of molten niobium pentafluoride. The quality of the spectrum was not high, but the pattern closely resembles that of the solid and, to a lesser extent, that of the low-temperature gas-phase spectra. In particular, if the analogue

[*] Despite spectroscopic evidence,[13] monomeric vanadium pentafluoride is probably not a rigorously D_{3h} species.[14] IF_5 which is of C_{4v} symmetry shows two strong polarised bands in the gas phase.[15]

[11] I. R. Beattie, J. R. Horder, and P. J. Jones, *J. Chem. Soc.* (*A*), 1970, 329.

[12] L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, 1967, **46**, 2402.

[13] H. H. Claassen and H. Selig, *J. Chem. Phys.*, 1966, **44**, 4039; H. Selig, J. H. Holloway, J. Tyson, and H. H. Claassen, *J. Chem. Phys.*, 1970, **53**, 2559.

[14] T. R. Dyke, A. A. Muenter, W. Klemperer, and W. E. Falconer, *J. Chem. Phys.*, 1970, **53**, 3382; note also that $[Nb(NMe_2)_5]$ is a square pyramid (C. Heath and M. B. Hursthouse, *Chem. Comm.*, 1971, 143).

[15] H. Selig and H. Holzman, *Israel J. Chem.*, 1969, **7**, 417; L. E. Alexander and I. R. Beattie, *J. Chem. Soc.* (*A*), 1971, 3091.

TABLE 2

Vibrational spectra of gaseous niobium and tantalum pentafluorides.* The i.r. spectrum of molten niobium pentafluoride (frequencies in cm^{-1})

NbF_5			TaF_5	
Melt † (110°)	Gas		Gas	
Infrared	Infrared ‡	Raman §	Infrared ‡	Raman §
		757s,pol	751w	752s,pol
767sh	749s		740w	
745sh	734s			
		[727pol]		[742pol]
			716s	716w
			703s	
705vs,br	689s	687m,pol	690s	693w,pol
679m				
495s,br	510m,br		522ms,br	
460s,br		253mw		254w
		210w		220w
		~170vw?		120w
		~130?		

* Bands in square brackets occur only on increasing the temperature and are assigned to monomer. † This spectrum, like that of the solid, was of poor quality. There may be a weak band at 652 cm^{-1}. ‡ Pressure in the region of 5 mmHg; temp. *ca.* 100 °C. § Calculated pressure for monomer at 400 °C *ca.* 5 atm. for NbF_5 and approximately 3 atm. for TaF_5.

of the 689 cm^{-1} band in the spectrum of the gas is considered to dominate the spectrum of the liquid as a broad band, the bands at 749 and 734 cm^{-1} in the gas may be correlated with shoulders in the liquid at 767 and 745 cm^{-1} respectively. The supposed bridge mode at 510 cm^{-1} in the gas correlates closely with the assignment of a bridge mode in the solid at 514 or 479 cm^{-1} and in the liquid at 495 and 460 cm^{-1}.

EXPERIMENTAL

Niobium pentafluoride and tantalum pentafluoride were prepared by the fluorination of the metal at 300 °C followed by several sublimations *in vacuo*.

Molecular Weight Studies.—The apparatus consisted of a 200 ml round-bottomed flask fitted with a 1 mm capillary tube projecting 5 cm into the flask and leading to a spiral gauge, a thermocouple pocket, and a 1 cm diameter tube containing a plunger fitted with O-rings to give a vacuum seal. The O-rings were lightly greased with silicone.

In operation a known weight (50—250 mg) of the material under investigation is sealed into a fragile glass ampoule which is suspended from the plunger in the raised position so that the ampoule is outside the furnace enclosing the bulb. The flask is equilibrated at the required temperature and dry nitrogen admitted to a pressure of *ca.* 150 mmHg. (The presence of the nitrogen is required to reduce the diffusion and sublimation to the spiral gauge connections external to the furnace.) At equilibrium the plunger is pushed down, smashing the ampoule and contents into the bulb. At the bottom of the stroke the plunger effectively seals the 1 cm side tube at a position approximately level with the outside of the flask. A steady pressure is rapidly attained, usually in less than 1 min. The apparatus was calibrated by use of blank experiments with no compound. The cell was checked with hexachloroethane, aluminium trichloride, and aluminium tribromide. In all cases the observed result lay within ±10% of the expected value.

Spectra.—I.r. spectra were studied with a Beckman IR11 instrument. Raman spectra were obtained with a Spex 1401 monochromator and a Spectra Physics 140 Argon ion laser.

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