Vapour Density and Vibrational Spectra of $MoOF_4$ and WOF_4. The Structure of Crystalline WOF_4

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Vapour density measurements on $MoOF_4$ show this compound to be monomeric in the gas phase. Similar measurements on WOF_4 show it to be essentially monomeric as a gas, although some association may occur at lower temperatures and higher pressures. Gas-phase Raman spectra of WOF_4 are invariant in the range 200—600° and closely similar to those of the melt and solid. The results demonstrate that solid WOF_4 is not principally an oxygen-bridged polymer. The spectra of $MoOF_4$ are closely similar to those of WOF_4 in all phases. Detailed studies of the gas-phase and matrix-isolated vibrational spectra of WOF_4, including structure of gas phase i.r. bands and Raman depolarization data, strongly suggest that the molecule is a square pyramid with an apical oxygen.

THE structure of oxide halides in the solid state, as melts, and as gases is of interest from the point of view of the discrete molecules as well as the nature of any polymerization behaviour. X-Ray structural studies on VOF_3,[1] WOF_4,[2] $MoOF_4$,[3] $ReOF_4$,[4] and $TcOF_4$ [5] show an approximately octahedral distribution about the metal in the

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solid state. WOF_4 is unique in that it has been suggested[2] that polymerization occurs *via* oxygen bridges whereas for the other compounds fluorine bridging is present. However, the distinction between oxygen and fluorine by X-ray crystallography in the presence of a heavy metal atom such as tungsten is difficult and spectroscopic measurements suggest that WOF_4 is fluorine-bridged in the solid state.[6,7] It has been pointed out[1] that the boiling (or sublimation) point sequence $VF_4 > 150°$, VOF_3 110°, CrO_2F_2 29·6° can be explained as due to the weakening of bonds *trans* to multiply-bonded oxygen[8] assuming the compounds to be similar in structure. Similar considerations[9] apply to: NbF_5 235°, $MoOF_4$ 186°; and to TaF_5 229°, WOF_4 185·9° (assuming this compound to be fluorine-bridged). The b.p. of these oxide fluorides, when compared with the boiling point of 73° for $ReOF_5$[9] for example, suggest polymerization in the melt as found for the two pentafluorides[10] mentioned.

TABLE 1

Gas phase molecular weights for WOF_4 and $MoOF_4$

Temp. (°C)	Wt. taken (g)	Apparent mol. wt.	Ratio
	WOF_4 (mol. wt. 276)		
242	0·0718	320	1·16
246	0·4253	332	1·20
253	0·1929	296	1·07
271	0·0930	288	1·04
289	0·3054	305	1·10
356	0·0802	298	1·08
	$MoOF_4$ (mol. wt. 188)		
231	0·0465	189	1·00
301	0·1313	175	0·94
314	0·0535	176	0·94
414	0·0551	185	1·00

Molecular weight data (Table 1) suggest that both WOF_4 and $MoOF_4$ are essentially monomeric gases, although for WOF_4 there is the possibility of some polymerization at lower temperatures and higher pressures. In particular all the results lie within the expected[10] ±10% of the monomer value except for two values for WOF_4. These occur for the lowest temperatures used for this compound and, in the case of the greatest deviation (ratio of apparent to true molecular weight 1·20) occur for the highest sample weight. In assessing the accuracy of these results it must be remembered that highly reactive compounds are being studied at temperatures up to 400°.

TABLE 2

Vibrational spectrum of WOF_4

Infrared				Raman			
	Matrix						
Solid	N_2	Ar	Gas	Gas	Matrix N_2	Melt	Solid *
1053m	(cut off 800 cm^{-1})		1055m *PQR*	1057s,pol	1057vs	1056vs,pol	1058vs
						1010w,pol?	
							744m
733w	728w	731mw	733m *PQR*	732vs,pol	727vs	730s,pol	728vs
						680vw	
675s	686s	691s	698vs *PQR*				
				631vw,br	630s		663mw
555m							
527sh						520w,pol	
				328w,br,sh	327m		330m,sh
(cut off 300 cm^{-1})					309m		318m,sh
		302w	298vw *PR*	301mw	304m	312m	314s
				291w	275m		
		246w	248w,sh	248w,pol			
		233mw	236mw *Q*	234w		242w	242mw
							215mw
	(cut off 200 cm^{-1})						

* Main bands only.

Table 2 summarizes vibrational i.r. and Raman data for WOF_4. The Raman spectrum of gaseous WOF_4 is invariant (for our experimental observations) in the range 200—600°. It is clear from the results of Table 2 that the W=O stretching frequency[11] is almost independent of phase. As the gas is monomeric with terminal oxygens this shows unambiguously that neither the solid nor the melt is principally oxygen-bridged. If we adopt the most likely fluorine-bridged model,[7] the molecule has C_{4h} symmetry and the stretching modes for the bridging fluorines are given by:

$$\Gamma_{\text{mol}} = a_g + b_g + e_u$$

The Raman-active modes a_g and b_g clearly resemble the a_{2g} and b_{1g} bridging-modes of the niobium pentafluoride tetramer.[12] For niobium pentafluoride the bands are respectively forbidden and weak. It is thus probable that the bridge modes of WOF_4 for the assumed structure would be weak in the Raman effect. The bridging mode of α-BiF_5 has been assigned[12] at 450 cm^{-1}. In the i.r. spectrum of solid WOF_4 there is a medium intensity

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band at 550 cm^{-1} which we assign to be a bridging fluorine mode. This band is absent in our gas-phase i.r. spectrum. The spectroscopic results on solid WOF_4 can thus be satisfactorily interpreted on a terminal-oxygen bridge fluorine model.

In the gas phase three molecular symmetries may be considered for a MOF_4 species. These are (a) C_{4v}, a square-based pyramid with an apical oxygen atom; (b) C_{3v}, a trigonal bipyramid with the oxygen atom in an axial position; (c) C_{2v}, trigonal bipyramid with the oxygen atom in an equatorial position. The normal vibrational modes for these point groups are as follows.

(a) $3a_1$ (R + i.r.) + $2b_1$ (R) + b_2 (R) + $3e$ (i.r. + R)

(b) $4a_1$ (R + i.r.) + $4e$ (R + i.r.)

(c) $5a_1$ (R + i.r.) + a_2 (R) + $3b_1$ (R + i.r.) + $3b_2$ (R + i.r.)

a_1 Modes are formally polarized in the Raman spectrum for all point groups. Observation of the vibrational spectra permits, in principle, a choice to be made between these three possibilities, though it would be very difficult to distinguish C_{2v} symmetry from a point group of even lower symmetry.

The gas-phase i.r. spectrum shows six bands in the region 90—1200 cm^{-1}, all of which may be considered as fundamental frequencies, while the gas-phase Raman spectrum shows eight bands, of which three are polarized. All the i.r. bands except one are coincident within experimental error with Raman bands. The matrix-isolation i.r. spectra show the same features as those observed in the gas phase, indicating that none of the gas-phase bands is a hot band, and that the rotational fine structure has probably been interpreted correctly. Diffusion experiments indicated that monomeric species had been originally isolated in the matrix; the two main sharp i.r. bands at 731 and 691 cm^{-1} were observed to decrease in intensity together, while a new broader feature appeared at 672 cm^{-1}. The matrix-isolation Raman spectrum although of only moderate quality, showed seven bands.

These results strongly suggest that the molecular symmetry is C_{4v}. Nine bands are observed, all of which can be regarded as fundamental frequencies. Three are Raman-polarized, and there are five coincidencies between the i.r. and Raman spectra. Of particular significance in making a choice between point groups is the observation of only two intense bands in the i.r. spectrum in the region near 700 cm^{-1}, both of which may be taken as due to tungsten–fluorine stretching modes. In the Raman effect for the 700 cm^{-1} region only one intense band is seen, coincident with the weaker of the two i.r. bands and polarized. A C_{2v} molecule, such as SOF_4,[13] SF_4,[14] or SeF_4 [15] is expected to show four 'tungsten–fluorine stretching modes,' two intense polarized bands in the Raman effect and the other two bands intense in the i.r. spectrum with possibly a third band coincident with a Raman mode. For a C_{3v} molecule, one anticipates one intense Raman band and one (non-coincident) intense i.r. band, together with a third, weaker band, present in both spectra. The situation obtaining in the present case, however, is analogous to that found in the well established C_{4v} molecule $XeOF_4$.[16] The one discrepancy between the observed spectra and the predictions of group theory is that the strongest band in the i.r. spectrum, at 698 cm^{-1}, is not observed in the Raman spectrum. This band is presumably due to an antisymmetric tungsten–fluorine stretching motion, which is anticipated to be a very weak Raman scatterer. One must also note that for none of the likely molecular symmetries are there modes which are i.r.-active but Raman-inactive.

The assignment of the observed bands to the nine fundamental modes of a C_{4v} molecule is largely straightforward. The three Raman-polarized bands at 1055, 733, and 248 cm^{-1} are the three a_1 modes, and may be identified with motions approximately described as the tungsten–oxygen stretching mode, the symmetric tungsten–fluorine stretching mode, and the symmetric deformation ('umbrella mode') of the OWF_4 framework. The three remaining bands observed in the i.r. spectrum are the e modes, of which that at highest frequency, 698 cm^{-1}, may be described as the antisymmetric tungsten–fluorine stretching mode. It is not clear which of the two remaining e modes, namely the antisymmetric in-plane and out-of-plane fluorine deformations will be at higher frequency. Previous investigations of C_{4v} molecules have generally assigned the higher frequency mode as the out-of-plane deformation,[17] and that procedure is followed here.

There are three further modes to be assigned, distributed as $2b_1 + b_2$. The highest frequency of these, at 631 cm^{-1}, is readily identified with the b_1 stretching mode ν_4. It is not easy to assign the b_1 and b_2 deformations. No clear pattern as to their relative intensities has emerged from earlier studies on C_{4v} oxide fluorides,[17] but the higher-frequency mode has generally been taken as the b_2 deformation. Following this tradition, we assign ν_5 at 291 cm^{-1} and ν_6 to the shoulder at 328 cm^{-1}.

It remains to discuss the shapes of the bands observed in the gas-phase i.r. spectrum. These provide further support to the assignment of C_{4v} molecular symmetry, although the extent of the support must not be overemphasized since in dealing with heated samples the possibility of the observed band shape being distorted by hot bands is very real. The 1055 and 733 cm^{-1} bands are observed to be virtually symmetrical, with

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broad P and R branches and a sharp, intense, Q branch. At 130° C, the P—R separation is measured as 20 (± 2) cm^{-1} for both bands. The molecular model chosen to predict band shapes has dimensions W=O 1·62, W–F 1·83 Å, O–W–F = 100°, as suggested by the crystal structure study and by comparison with related molecules.[18-22] For this structure, the moments of inertia are $I_A = I_B = 172$ a.m.u. Å^2, $I_C = 245$ a.m.u. Å^2, giving $\beta = I_A/I_C - 1 = -0{\cdot}30$. The predicted P—R separation[23] at 130 °C is 21·5 cm^{-1}, in fair agreement with the observed value. It is further predicted that the Q branch of parallel bands would be more intense than the P and R branches, again as observed. For a C_{2v} molecule, with dimensions similar to those above or within a fairly large range of them, the W–O direction would be parallel to the intermediate moment of inertia, leading to a ' type b ' band for the W–O stretching mode, in contrast to the simple ' type a ' band observed.

Coriolis coupling coefficients can be determined from the contours of i.r. perpendicular bands.[24] It is known[25] that for a C_{4v} molecule of the type ABC$_4$, the sum of the coefficients ξ_7, ξ_8, and ξ_9 should be $I_C/2I_A$, or 0·70 for the structure proposed. The values determined here are $\xi_7 = 0{\cdot}18\ (\pm\ 0{\cdot}06)$, $\xi_8 = 0{\cdot}60\ (\pm\ 0{\cdot}03)$, $\xi_9 = -0{\cdot}15\ (\pm\ 0{\cdot}10)$, whose sum is 0·63 (± 0·12), in fair agreement with the theoretical value. The estimated standard deviations represent uncertainties due both to the choice of a model structure, and to experimental measurements. The particularly large uncertainty for ξ_9 is caused by ν_3 overlapping ν_9.

The gas-phase infrared spectrum of WOF$_4$ has already been partially investigated, with conflicting results.

Ward and Stafford[26] examined the region 1000—400 cm^{-1}, but, remarkably, found only a series of bands in the region 554—576 cm^{-1} and W=O at 1030 cm^{-1}. The work of Edwards and Jones,[2] and of Blanchard,[27] gave bands near 1055, 733, and 698 cm^{-1}, as found here, but both groups also reported further absorptions not detected here for fresh samples. We observed that prolonged heating of WOF$_4$ in borosilicate cells caused new i.r. bands to appear at *ca.* 720, 630, and 560 cm^{-1}. These new bands are therefore presumably due to decomposition and reaction products of WOF$_4$.

The gas-phase and matrix spectra observed for MoOF$_4$ are presented in Table 3. It is immediately apparent that they closely resemble those of WOF$_4$, and we have assigned them by analogy (Table 4). In general the spectra obtained for MoOF$_4$ are of poorer quality than for the tungsten compound; we ascribe this to the plethora of naturally occurring isotopes of molybdenum (seven species of significant abundance between mass numbers 92 and 100) leading to broad bands, and to the substantially greater reactivity of MoOF$_4$ than WOF$_4$, which led to more severe problems of corrosion. The chief difference in the spectra of the two compounds is the observation of only one intense band near 700 cm^{-1} for MoOF$_4$, which we attribute to an accidental near coincidence of ν_2 and ν_7; we have taken ν_2 as the peak of Raman scattering and ν_7 as the maximum of i.r. absorption. The matrix-isolation i.r. contours of this absorption at 716 cm^{-1} are very complex, and are consistent with the presence of two overlapping bands, but the complications introduced by the many Mo isotopes, and by possible site effects, make detailed analysis of this band unprofitable.

TABLE 3

Vibrational spectrum of MoOF$_4$

Infrared		Raman	
Matrix Ar	Gas	Gas	Melt
(cut off 800 cm^{-1})	1048m *PQR*	1047m,pol	1039s,pol
716s	720vs,br		
		714s,pol	713s,pol
			666m,pol
			506vw
301w	294w *PQR*	308m,br	311m
259m	264w *PQR*		
233m	236w *PR*		240wbr
(cut off 200 cm^{-1})			

TABLE 4

Assignment of fundamental frequencies of the monomeric molecules (in cm^{-1})

Mode	Symmetry	WOF$_4$	MoOF$_4$
ν_1	a_1	1055	1048
ν_2	a_1	733	714
ν_3	a_1	248	264
ν_4	b_1	631	
ν_5	b_1	328	
ν_6	b_2	291	
ν_7	e	698	720
ν_8	e	298	294
ν_9	e	236	236

Finally we note that using fluorine bridges the packing of the gas-phase square pyramidal WOF$_4$ monomers to form a tetrameric species leads inevitably to the ' most probable structure ' given by Bennett, Haas, and Purdham.[7]

EXPERIMENTAL

Compounds were prepared as described previously.[6] The sapphire cell was similar to that recently reported[15b] except that a high temperature gold O-ring seal was introduced.[28] For the i.r. studies a cell with diamond windows was used.[28]

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