Infrared and Electronic Spectra of Matrix-isolated Tetrafluoro- and Tetrachloro-oxo-molybdenum(VI) and -oxotungsten(VI) and Tetrabromo-oxotungsten(VI)

By **William Levason,* Ramaier Narayanaswamy, J. Steven Ogden,* Antony J. Rest,*** and **Jeremy W. Turff,** Department of Chemistry, The University, Southampton SO9 5NH

The prominent i.r. bands of the title compounds isolated as monomers in low-temperature matrices have been obtained. Some anomalies in the literature regarding the fundamentals of $WOCl_4$ have been resolved, and in particular, it is shown *via* high-resolution studies, that whilst argon matrices generally yield multiple trapping sites, nitrogen matrices typically produce only one site. Electronic spectra in N_2 matrices have been recorded for all five compounds and compared with the predictions of $X\alpha$ calculations. The matrix electronic spectra are shown to be superior to gas-phase spectra in terms of resolution, the observation of vibrational fine structure, and the absence of any complications due to the possible presence of decomposition products.

FIVE oxide tetrahalides of molybdenum(VI) and tungsten(VI) have been prepared and structurally characterised in the solid state, *viz.* $MoOF_4$, $MoOCl_4$, WOF_4, $WOCl_4$, and $WOBr_4$. All contain a distorted six-co-ordinate arrangement about the metal. In $MoOF_4$ the structure consists of infinite chains with *cis*-fluorine bridges,[1] while WOF_4 is a fluorine-bridged tetramer [2] not an oxygen-bridged molecule as originally reported.[3] Molybdenum(VI) oxide tetrachloride contains square-pyramidal molecules weakly associated as dimeric units *via* chlorine bridges.[4] In contrast, $WOCl_4$ and $WOBr_4$ are *trans*-oxygen-bridged polymers.[5] In the gas phase, electron diffraction,[6-8] i.r. and Raman spectroscopy,[9-11] and mass spectrometry [10,12] have shown that the major species present are five-co-ordinate square-pyramidal monomers with C_{4v} symmetry. Evidence for the existence of $MoOBr_4$ and the oxide tetraiodides is tenuous, although Ward and Stafford [9] suggested that new i.r. bands observed in the vapours over MO_3–LiX (M = Mo or W; X = halide) melts could be due to $MoOBr_4$ and WOI_4.

There is considerable recent interest in the existence of MOX_4 species in the gas phase, not least because of the presence of such species in lamps in which traces of halogens and/or halocarbons have been added to the noble-gas lamp atmospheres. As part of an investigation of simple monomeric transition-metal oxohalides using matrix-isolation spectroscopy, *e.g.* $CrOCl_3$,[13] we report here a study of the monomeric MOX_4 species, isolated in noble-gas matrices, employing high-resolution i.r. spectroscopy and electronic spectroscopy. Such studies [14] have a number of important advantages over gas- and solution-phase studies: (*a*) the matrix sampling technique results in well isolated monomeric molecules with no significant interference from dimers or impurities, (*b*) narrow linewidths in the i.r. spectra allow the structure of the species to be deduced unambiguously because isotopic splitting patterns can be resolved, and (*c*) the low temperatures and the isolation of molecules are the most favourable for the observation of vibrational fine structure in electronic spectroscopy.

During the course of this work two reports appeared describing the analysis of the electronic spectra of some MOX_4 species in high-temperature vapours on the basis of SCF-$X\alpha$-SW calculations using the overlapping atomic sphere model.[15,16] In particular, assignments for $MoOCl_4$,[15] $WOCl_4$,[15,16] and $WOBr_4$ [15,16] were made and may be compared with the results described in our experiments. An electronic spectrum of $MoOCl_4$ in CCl_4 solution has also been reported.[17]

EXPERIMENTAL

Preparation of Compounds.—The compounds $MoOF_4$ and WOF_4 were prepared by the reaction of MO_3 and F_2 in a flow system.[18]

The compounds $MoOCl_4$ [%Cl: 55.6 (found), 55.9 (calc.)] and $WOCl_4$ [%Cl: 41.0 (found), 41.5 (calc.)] were prepared by the reaction of MO_3 with thionyl chloride under reflux followed by vacuum sublimation.[19] The compound $WOCl_4$ was also conveniently prepared [20] from WO_3 and BCl_3 in a manner analogous to that used to prepare $WOBr_4$ (see below).

$WOBr_4$. Purified WO_3 (*ca.* 3 g) was placed in an ampoule, attached to a vacuum line, and evacuated. A small quantity of BBr_3 was condensed onto the trioxide using liquid nitrogen and the ampoule allowed to warm slowly in an ice-bath.† As the ampoule warmed a vigorous exothermic reaction occurred and a black solid was produced. This procedure was repeated until some BBr_3 remained unreacted, then the ampoule was evacuated, sealed, and the products vacuum sublimed. The product, $WOBr_4$ [%Br: 61.5 (found), 61.5 (calc.)], was a black lustrous solid.

All reagents ($SOCl_2$, BCl_3, BBr_3, $Na_2[WO_4]$, and $[NH_4]_2[MoO_4]$) were obtained from B.D.H. Chemicals Ltd. The boron halides were distilled under vacuum before use. Commercial samples of MoO_3 and WO_3 were found to be relatively unreactive and so fresh samples were prepared as follows. The compound MoO_3 was prepared by the thermal decomposition of $[NH_4]_2[MoO_4]$ at *ca.* 200 °C. For WO_3, a solution of $Na_2[WO_4]$ was acidified with HCl and the resultant precipitate was filtered off, washed with distilled water, and dried in an oven at 120 °C.

Matrix-isolation Spectroscopy.—All samples were vacuum resublimed immediately before use and were vaporised

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† **CAUTION:** The use of large amounts of BBr_3 or the omission of the ice-bath can result in an explosion.

from Pyrex break-seal ampoules, where necessary equipped with a poly(tetrafluoroethylene) stopcock [Youngs (Acton) Ltd.]. The vapours were co-condensed with the appropriate matrix gas (B.O.C. Special Gases Ltd.) on to a CsI window for i.r. studies, or a LiF window for u.v.–visible studies, attached to a closed-cycle liquid helium refrigerator (Air Products and Chemicals Ltd., CSW-202 Displex) in a high-vacuum (10^{-6} Torr)* cryostat. Deposition times varied in the range 5—30 min. For i.r. studies the spray-on temperatures of the samples ($MoOF_4$ and WOF_4, 25 °C; $MoOCl_4$, 25—40 °C; $WOCl_4$, 60 °C; $WOBr_4$, 300 °C) were higher than those required for u.v.–visible studies (20, 20, 40—50, 120—160 °C) because of the lower absorption coefficients of the i.r. bands. Perkin-Elmer models 225 and 580B spectrometers, for i.r. studies, and a Pye-Unicam SP 1800B spectrometer, for u.v.–visible studies (200—850 nm), were regularly calibrated with the appropriate standard reference materials.

TABLE 1

Infrared bands (cm^{-1}) and assignments for monomeric MOX_4 species

Fundamental modes	WOF_4			$MoOF_4$			$WOCl_4$		$MoOCl_4$		$WOBr_4$	
	N_2[a]	Ar[a]	gas[a]	N_2[a]	Ar[a]	gas[b]	N_2[a]	gas[d]	N_2[a]	gas[c]	N_2[a]	gas[e]
$\nu_1(A_1)$	1 058[f]	1 053[f]	1 055	1 050[f]	1 045[f]	1 048	1 032[f]	1 027	1 017[f]	1 015	1 025	1 004
$\nu_2(A_1)$	726	729	733	714	719	714	400	405				
$\nu_3(A_1)$	254	245	248	267	258	264						
$\nu_7(E)$	686	690	698	708[f]	712[f]	720	380[f]	383	395[f]	404	264	265
$\nu_8(E)$	309/304	301	298	309/304	301	294	260[g]	260[g]				
$\nu_9(E)$	236	232	236	238	232	236		145[g]				

Isotope fine structure for $MoOF_4$[h]

Band	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
ν_1 (Mo=O), N_2 matrix	1 052.9	1 051.1	1 050.3	1 049.4	1 048.6	1 047.8	1 046.2
ν_1, Ar matrix, site A	1 047.9	1 046.0	1 045.2	1 044.4	1 043.6	1 042.8	1 041.3
ν_7 (Mo–F), site A	716.5	714.4	713.3	712.3	711.3	710.3	708.4

[a] This work: estimated matrix ratios *ca.* 1 : 1 000. [b] Ref. 11. [c] Refs. 11, 21, and 23. [d] Refs. 24 and 25. [e] Refs. 9 and 23. [f] Centre of complex absorption. [g] Tentative assignment. [h] These isotope frequencies, together with the other observed stretching modes, may be fitted to better than 0.1 cm^{-1} using several force fields. In particular, the calculated line diagram accompanying Figure 1(*b*) employs three independent parameters $F_R = 8.813$, $F_r = 4.318$, and $F_{rrcis} = 0.485$ mdyn $Å^{-1}$, together with the constraints $F_{rrtrans} = 0.5\ F_{rrcis}$ and $F_{Rr} = -0.1\ F_{rrcis}$ (R = Mo–O, r = Mo–F) (1 dyn = 10^{-5} N).

RESULTS AND DISCUSSION

Infrared Studies.—(*a*) $MoOF_4$ *and* WOF_4. The vibrational spectra previously obtained for these species leave little doubt that in the *vapour* phase the predominant species is the monomer, with symmetry C_{4v}. For this structure, $\Gamma_{vib.} = 3A_1$ (i.r., R) $+ 2B_1$ (R) $+ B_2$ (R) $+ 3E$ (i.r., R) and Beattie and co-workers [11] in particular have assigned the *i.r.-active* bands in vapour-phase WOF_4 as A_1 1 055, 733, and 248 cm^{-1} and E 698, 298, and 236 cm^{-1}. These authors also studied WOF_4 in low-temperature matrices under medium resolution, and noted corresponding bands (cm^{-1}) at 1 057 (N_2), 727 (N_2), 246 (Ar), 691 (Ar), 302 (Ar), and 233 (Ar).

Our spectra in nitrogen and argon matrices were very similar (Table 1), but under high resolution several of our argon-matrix bands were accompanied by weak shoulders separated by up to 5 cm^{-1} from the principal absorption. In nitrogen, the bands were generally much cleaner, and a tungsten isotope pattern was just discernible on the W=O stretching mode at 1 058 cm^{-1} [Figure 1(*a*)]. However, the degenerate bending mode ν_8 appeared as a distinct doublet at 309 and 304 cm^{-1}, and although there was no evidence for dimerisation or sample decomposition, it would appear that the nitrogen matrix environment produced a slight distortion from C_{4v} symmetry.

The results for $MoOF_4$ were also in good agreement with the literature, and entirely consistent with the isolation of monomers. Table 1 compares our matrix frequencies with the gas-phase fundamentals reported by Beattie and co-workers,[11] and the only significant perturbation (under low resolution) is the splitting again observed for ν_8 in a nitrogen matrix. For this system, however, isotope effects due to the central metal atom are easier to resolve, and the nature of possible ' matrix effects ' thus probed in more detail.

Figure 1(*b*) shows a nitrogen-matrix spectrum of the Mo=O stretching mode under high resolution. The seven prominent isotopes of molybdenum are well resolved, and the accompanying line diagram indicates the extent of spectral agreement with calculations based on a simple force field (Table 1). In contrast, Figure 1(*c*) shows the same mode in argon, and it is evident that more than one trapping site must be invoked to interpret this pattern. A similar effect is also observed for the intense Mo–F stretching mode at *ca.* 710 cm^{-1} (ν_7, E). Figure 1(*d*) shows the relevant spectral region under high resolution, and again the observed spectrum is readily interpreted as two overlapping septets. The relative intensities of the two patterns are similar to those associated with the Mo=O mode, and this provides very strong evidence for multiple site trapping.[13,14] As the lower-frequency mode is doubly degenerate, these spectra also indicate that both these trapping sites (A and B) have relatively high symmetry, as no splitting of the degeneracy could be detected. In contrast, the *nitrogen*-matrix spectrum of this region showed a broad band for which we were unable adequately to resolve isotope fine structure. We believe that this is because of a slight

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* Throughout this paper: 1 Torr — 101 325/760) Pa.

lifting of degeneracy, the effects of which are not as pronounced as for ν_8, but are sufficient to destroy resolution.

For both WOF_4 and $MoOF_4$ we therefore conclude that in nitrogen matrices there is essentially *one* trapping site of rather low symmetry, and that in argon there are at least two sites, neither of which causes a detectable lifting of degeneracy.

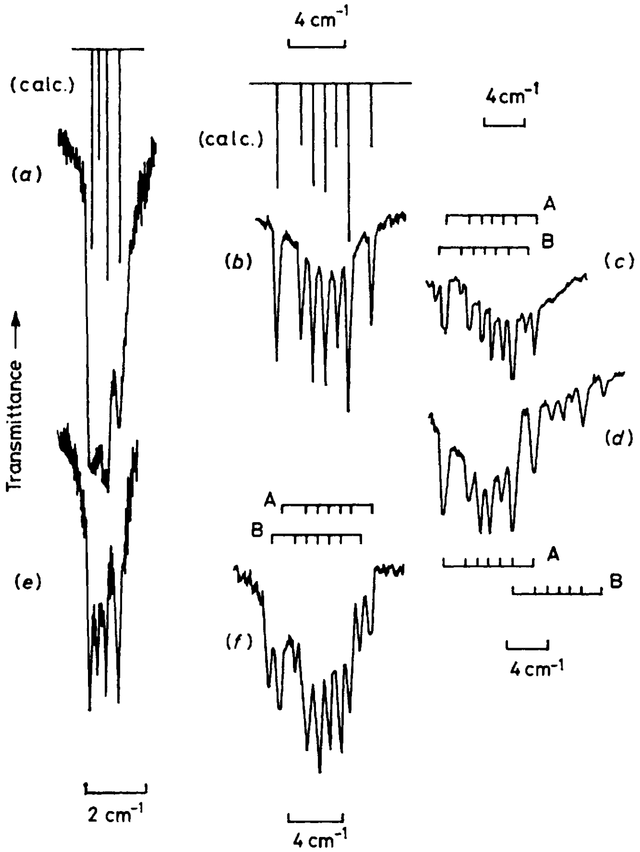

FIGURE 1 Observed and calculated isotope patterns in the i.r. spectra of matrix isolated MOX_4 species: (*a*) ν(W=O) in WOF_4 (N_2 matrix); (*b*) ν(Mo=O) in $MoOF_4$ (N_2 matrix); (*c*) ν(Mo=O) in $MoOF_4$ (Ar matrix) showing sites A and B; (*d*) ν(Mo–F) in $MoOF_4$ (Ar matrix) showing sites A and B; (*e*) ν(W=O) in $WOCl_4$ (N_2 matrix); (*f*) ν(Mo=O) in $MoOCl_4$ (Ar matrix) showing sites A and B

(*b*) $WOCl_4$ *and* $MoOCl_4$. By comparison with the oxyfluorides of tungsten and molybdenum, vibrational data on monomeric $WOCl_4$ and $MoOCl_4$ are considerably less extensive, although a C_{4v} structure has been established for both species. Beattie and co-workers [11] studied the Raman and i.r. spectra of the vapours at 180—200 °C, and although $MoOCl_4$ was too intensely coloured to yield results, they report Raman bands for $WOCl_4$ at 1 027 and 402 cm^{-1} and i.r. bands at 1 027, 404vw, 383s, and 358w cm^{-1}. Bues *et al.*[21] have obtained Raman data for $WOCl_4$ in all three phases, and their assignments were subsequently used by Brockner and Hovdan [22] to calculate the vibration frequencies of the various isotopic $WOCl_4$ monomers. Unfortunately, these calculations were based on fundamentals obtained from different phases, and this led to a tabulation of i.r.-active ($A_1 + E$) modes for $WOCl_4$ of A_1 1 028.0, 407.6, and 161.7 cm^{-1} and E 337.4, 265.4, and 149.9 cm^{-1}. These frequencies agree quite well with the four vapour-phase bands reported by Bues, at 1 025w, 407s, *ca.* 260w, and *ca.* 145w cm^{-1}, but the prediction of a highest E mode at 337.4 cm^{-1} is considerably lower than the value (*ca.* 383 cm^{-1}) found experimentally by Beattie.[11] The position of this mode (ν_7) has subsequently been confirmed by Mal'tsev and co-workers,[23] in an independent i.r. study of the vapour, where they found, in addition, absorptions at 305 and 254 cm^{-1} which they attribute also to $WOCl_4$. A combination of these results thus leads to the following assignment for the i.r.-active fundamentals of $WOCl_4$: A_1 *ca.* 1 027 and *ca.* 405 cm^{-1}; E 383 cm^{-1}, with the weaker features at *ca.* 260 and 145 cm^{-1} being assigned either as the two remaining E modes or as A_1 and E.

Our nitrogen-matrix spectra for this system (Table 1) gave strong bands centred at *ca.* 1 032 and *ca.* 380 cm^{-1}, both of which showed fine structure, and two much weaker features at *ca.* 400 and *ca.* 260 cm^{-1}, whilst in argon a similar pattern of fundamentals was observed with additional site splittings. Figure 1(*e*) shows the multiplet structure on the band at 1 032 cm^{-1} (N_2 matrix) which corresponds closely to the pattern expected for a tungsten isotope effect. (The effect of different *chlorine* isotopes on this mode has been shown to be negligible.[22]) In the region of 380 cm^{-1}, the nitrogen-matrix spectrum shows four prominent bands under high resolution, at 384.2, 379.3, 375.2, and 371.4 cm^{-1}. However, the separation between these bands is too large to be attributed solely to a chlorine isotope effect,[21] and we believe that this fine structure probably arises from the removal of the degeneracy. The absence of other spectral features leaves little doubt that monomeric $WOCl_4$ has been isolated.

There are even less published data on monomeric $MoOCl_4$. Barraclough and Kew [24] report ν(Mo=O)-(A_1) at 1 015 cm^{-1}, whilst unpublished observations by Bukovsky [25] confirm this value and locate $\nu_7(E)$ at *ca.* 404 cm^{-1} for the vapour-phase molecule. Our matrix experiments yielded a deceptively simple spectrum under low resolution, and in nitrogen we observed two strong features at *ca.* 1 017 and 395 cm^{-1} with corresponding bands in argon at *ca.* 1 012 and *ca.* 399 cm^{-1}. However, under high resolution, it was evident that neither matrix provided a unique trapping site. Figure 1(*f*) shows the Mo=O stretching mode under high resolution in an argon matrix and the complicated pattern observed is rationalised by invoking two overlapping molybdenum isotope septets. The intense lower-frequency feature was similarly complex under high resolution, and typically comprised *ca.* 10 poorly resolved components separated by *ca.* 2 cm^{-1}. No attempt was made to analyse this pattern in view of the abundance of molybdenum and chlorine isotopomers, and the existence of multiple sites, but despite these complications, we are confident that the spectra show that monomeric $MoOCl_4$ has been isolated in Ar and N_2 matrices.

(*c*) $WOBr_4$. Spectroscopic data on monomeric $WOBr_4$ are also sparse. Ward and Stafford,[9] working in the KBr region (>400 cm^{-1}), assigned a prominent band at 1 004 cm^{-1} to this molecule in their study of high-temperature oxohalides of molybdenum and tungsten, whilst Mal'tsev and co-workers[23] reported an intense low-frequency band at 265 cm^{-1} in their far-i.r. studies (200—500 cm^{-1}). Our nitrogen-matrix spectra obtained from purified samples of $WOBr_4$ gave only two bands (Table 1). The most intense feature occurred at 264 cm^{-1} and the second band was observed at 1 025 cm^{-1}. Both bands were relatively narrow (*ca.* 3 cm^{-1}) and there were no obvious site effects. Attempts to resolve the tungsten isotope pattern on the higher-frequency band resulted in spectra of slightly poorer quality than those previously obtained for WOF_4 (and $WOCl_4$). However, there seems little doubt that monomeric $WOBr_4$ has also been satisfactorily isolated.

Ultraviolet–Visible Studies.—(*a*) *Spectra*. Previous attempts[15,16] to obtain electronic spectra of MOX_4 compounds in the gas phase have been fraught with uncertainties concerning disproportionation because of the high temperatures (>80 °C) needed to achieve a sufficient vapour pressure of the compounds to measure the spectra. For example, although mass spectrometric studies indicate that $MoOCl_4$,[12,24] $WOCl_4$,[12,24] and $WOBr_4$[12,25,26] vaporise as monomeric molecules, other studies indicate that $MoOCl_4$[27,28] dissociates as $2MoOCl_4 \longrightarrow 2MoOCl_3 + Cl_2$, and that $WOCl_4$[29-32] disproportionates in the vapour phase above 200 °C with the formation of WO_2Cl_2 and WCl_6. Some of the bands appearing in the gas-phase spectra above $MoOCl_4$ and $WOCl_4$ were therefore assigned[15,16] to Cl_2 ($MoOCl_4$) and WCl_6 ($WOCl_4$). In view of the weak association of $MoOCl_4$ molecules as dimers *via* chlorine bridges,[4] it seemed possible that the reported[17] solution spectrum of $MoOCl_4$ was not of monomeric $MoOCl_4$ molecules. Experiments to obtain the electronic spectra of MOX_4 molecules using the matrix-isolation technique do not require high temperature for vaporisation (see Experimental section); in fact lower vaporisation temperatures were required than for matrix i.r. spectra where isolation of monomeric species has been unambiguously established (see above).

The electronic spectra of matrix-isolated monomeric MOX_4 molecules [N_2 matrices,* *ca.* 1 : 2 000; Figure 2(*a*)—(*e*)] show a large number of bands, some with resolved vibrational fine structure. Band maxima positions † and vibrational spacings are given in Table 2. Unlike CrO_2Cl_2,[33-35] $VOCl_3$,[35] and MnO_3Cl[35] for which luminescence spectra have been obtained for the matrix-isolated molecules, no luminescence was detected on exciting any of the MOX_4 molecules in any of their electronic absorption bands.

(*b*) *Assignment of spectra*. Assignment of the electronic spectra can be attempted using molecular-orbital calculations[15,16,36] and from calculations of charge-transfer energies *via* optical electronegativities.[37]

TABLE 2

Observed[a] band positions [$\lambda_{max.}$/cm^{-1} (nm)] for MOX_4 compounds isolated in N_2 matrices at 12 K

Compound	Band position	Tentative assignment[b]
$MoOF_4$	44 250 (226.0)	
	39 150 (255.4)[c]	c.t. (F→Mo)
WOF_4	39 560 (252.8)[d]	c.t. (F→W)
$MoOCl_4$[e]	48 780 (205.0)	c.t. (Cl→Mo)
	36 630 (273.0)	c.t. (Cl→Mo)
	31 250 (320.0)	c.t. (O→Mo)
	20 790 (481.0)	c.t. (Cl→Mo)
	15 770 (634.0)[f]	c.t. (Cl→Mo)
	15 380 (650.0)[f]	c.t. (Cl→Mo)
$WOCl_4$[g]	44 840 (223.0)	c.t. (Cl→W)
	38 870 (257.3)[h]	c.t. (Cl→W)
	37 040 (270.0)	c.t. (O→W)
	33 330 (300.0)	c.t. (Cl→W)
	28 270 (353.7)	c.t. (Cl→W)
	26 320 (380.0)	c.t. (Cl→W)
	22 400 (446.5)	c.t. (Cl→W)
$WOBr_4$[i]	43 480 (230.0)	c.t. (Br→W)
	37 880 (264.0)	c.t. (O→W)
	35 460 (282.0)	c.t. (Br→W)
	33 110 (302.0)	c.t. (Br→W)
	31 250 (230.0)	c.t. (Br→W)
	29 410 (340.0)	c.t. (Br→W)
	25 970 (385.0)	c.t. (Br→W)
	20 830 (480.0)	c.t. (Br→W)
	17 830 (561.0)	c.t. (Br→W)
	15 110 (662.0)	c.t. (Br→W)

[a] Wavenumber positions obtained from spectra measured in wavelength (±0.2 nm). [b] See text, Table 3, and Figure 4; c.t. = charge transfer. [c] Vibrational progression: 41 390, 40 540, 39 870, 39 150, 38 580, 37 950, 37 370, 36 710, 36 100, 35 390, 34 690, 33 990, and 33 330 cm^{-1}; *i.e.* $\nu_{av}' = 670 \pm 70$ cm^{-1}. [d] Vibrational progression: 46 320, 45 600, 44 980, 44 390, 43 800, 43 100, 42 430, 41 700, 41 030, 40 180, 39 530, 38 790, and 38 120 cm^{-1}; *i.e.* $\nu_{av}' = 685 \pm 70$ cm^{-1}. [e] Band positions in CCl_4 solution: 37 200, 20 800, and 14 400 cm^{-1}; data from ref. 17. Band positions in gas phase: 37 040, 21 280, and *ca.* 15 400 cm^{-1}; data from ref. 15. [f] Treating this splitting (see text) as two resolved peaks of a vibrational progression would give a value of $\nu' = 440 \pm 50$ cm^{-1}. [g] Band positions in gas phase: 44 400, 27 800, and 20 830 cm^{-1}; data from ref. 15. [h] Vibrational progression: 39 450, 39 100, 38 870, 38 540, 38 240, 37 910, and 37 660 cm^{-1}; *i.e.* $\nu' = 300 \pm 70$ cm^{-1}. [i] Band positions in gas phase: 35 000, 22 000, 17 000, and 15 000 cm^{-1}; data from ref. 16.

The $X\alpha$ calculations[36] of the electronic energy levels in the d^1 ions $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$ suggest that the highest occupied orbital is the predominantly metal d_{xy} orbital ($2b_2$) and that below this are several levels ($1a_2$, $6e$, $3b_1$, $5e$, $7a_1$) which are essentially non-bonding since they are localised on the halogens. For the d^0 MOX_4 compounds the $2b_2$ level will be empty and all the absorption bands must involve ligand→metal charge-transfer transitions. The SCF-$X\alpha$-SW calculation[15,16] of the orbital populations and orbital energies for $MoOCl_4$, $WOCl_4$, and $WOBr_4$ is in agreement with the relative ordering of energy levels for the d^1 ions, although the C_{4v} symmetry designation of levels is different.

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* Nitrogen was used as a matrix because of the i.r. observations of single trapping sites.

† Absorption coefficients could not be measured because it was not possible to determine the amount of substrate in the beam of the spectrometer.

Figure 3 gives a tentative assignment of energy levels.

A consideration[37] of the charge-transfer energies and optical electronegativities for a range of related oxo-compounds of vanadium, molybdenum, tungsten, and niobium allows the calculation of the lowest-energy O→M and X→M (X = halogen) charge-transfer bands (Table 3). The charge-transfer bands would be expected to show vibrational progressions because the transfer of charge will alter the equilibrium geometry of the excited state with respect to the ground state. These progressions should be particularly informative in assigning bands because they will involve the excited state A_1 metal–halogen [ν(M–X)′] and metal–oxygen [ν(M–O)′] stretching modes and also the A_1 metal–halogen [δ(M–X)′] deformation modes, *cf.* the ν(Cr–Cl) and δ(Cr–Cl) progressions on the lowest-energy charge-transfer absorption bands and emission bands of CrO_2Cl_2.[33-35]

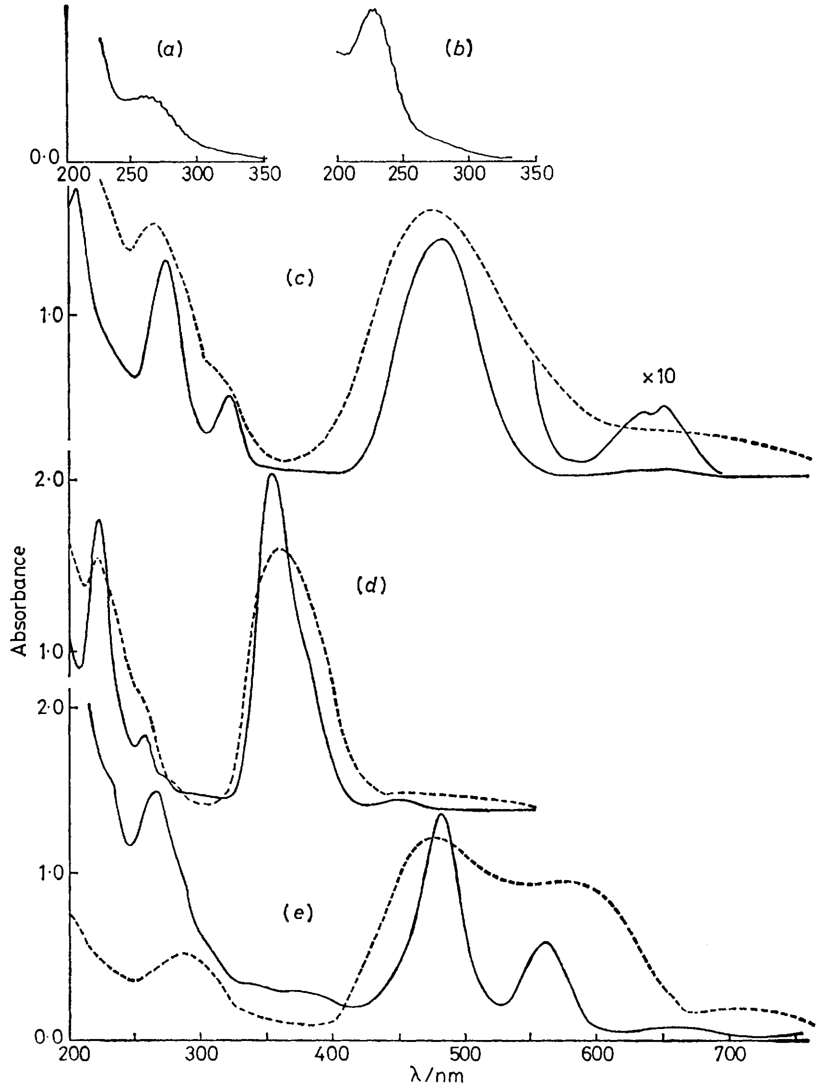

FIGURE 2 Electronic absorption spectra (——) for monomeric MOX_4 compounds isolated in N_2 matrices at 12 K: (*a*) $MoOF_4$, (*b*) WOF_4, (*c*) $MoOCl_4$, (*d*) $WOCl_4$, and (*e*) $WOBr_4$. Previously obtained gas-phase spectra (— — —) are included where these have been obtained (refs. 15 and 16)

The lowest-energy charge-transfer bands for $MoOF_4$ and WOF_4 (Figure 2, Table 2) are predicted to be O→M bands on the basis of optical electronegativities[37] (Table 3) and the ionisation and appearance potentials of ions observed by mass spectrometry.[12] However, the lowest-energy bands for $MoOF_4$ and WOF_4 show vibrational progressions ($\nu_{Mo}' = 670 \pm 70$, $\nu_W' = 685 \pm 70$ cm^{-1}) which are more comparable with A_1 ν(Mo–F) (714 cm^{-1}) and A_1 ν(W–F) (726 cm^{-1}) than with A_1 ν(Mo–O) (1 050 cm^{-1}) and A_1 ν(W–O) (1 058 cm^{-1}) vibrational modes. Furthermore, the absorption spectrum of MoF_6 shows a vibrational progression of 639 cm^{-1} which has been assigned to the A_{1g} ν(Mo–F)′ vibration in the excited state corresponding to a wavenumber of 736 cm^{-1} in the

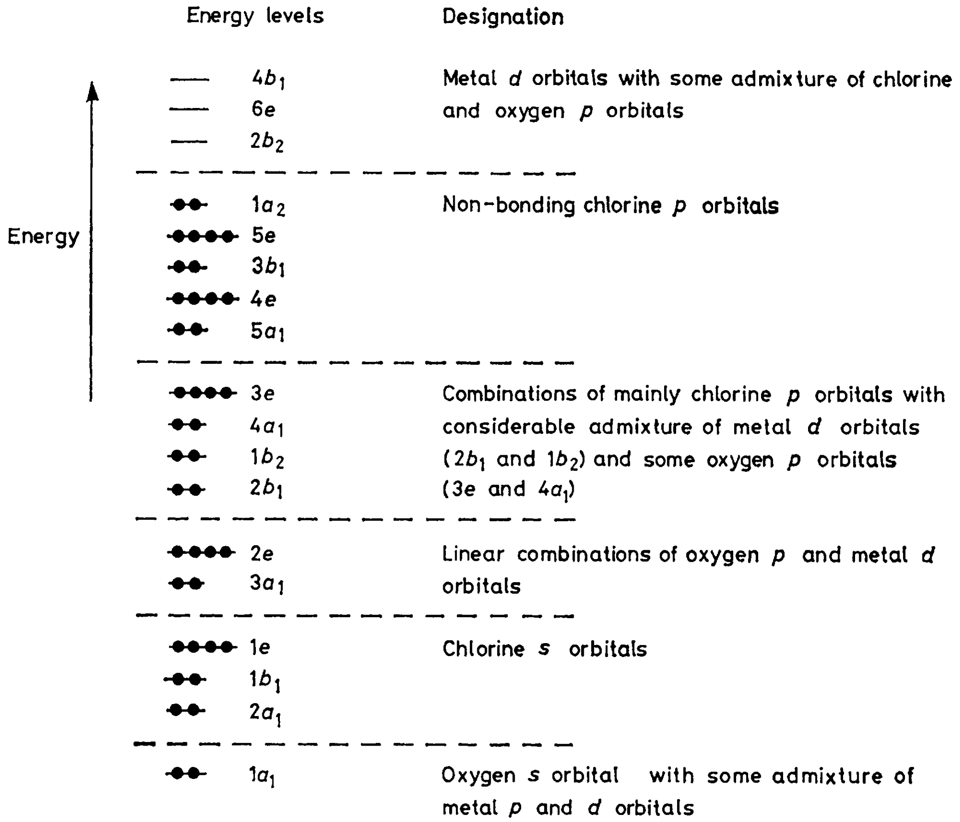

FIGURE 3 Schematic molecular-orbital energy diagram (based on refs. 15 and 16) for MOX_4 molecules showing occupancy of energy levels (● = electron) and their nature and C_{4v} symmetry designations

TABLE 3

Calculated [a] band positions (cm^{-1}) for the lowest-energy O→M and X→M charge-transfer (c.t.) transitions of MOX_4 compounds

Compound	c.t. (O→M)	c.t. (X→M)
$MoOF_4$ [b]	31 000 ± 2 000	42 000 ± 2 000
WOF_4 [b]	38 000 ± 2 000	49 000 ± 2 000
$MoOCl_4$	31 000 ± 2 000	15 000 ± 2 000
$WOCl_4$	38 000 ± 2 000	22 000 ± 2 000
$WOBr_4$	38 000 ± 2 000	14 000 ± 2 000

[a] Ref. 37. [b] Band positions obtained by using an optical electronegativity of 3.9 for F^- (C. K. Jorgensen, *Struct. Bonding* (*Berlin*), 1966, **1**, 3) in the expressions given in ref. 37.

ground state.[38] It seems reasonable, therefore, to assign the lowest-energy charge-transfer band to the $5e \rightarrow 2b_2$ fluorine→metal transition (Figure 3), analogous to the other MOX_4 compounds (see below), rather than to an oxygen→metal transition. Some inconsistencies have been noted previously for oxyfluorides,[37] *e.g.* while the lowest charge-transfer band of VOF_3 (25 700 cm^{-1}) [39] agrees with the calculated value (26 000 cm^{-1}), $[VOF_5]^{2-}$ shows the lowest-energy band at a considerably higher energy (31 000 cm^{-1}).[39] Further work on other oxyfluorides seems to be called for.

The lowest-energy bands for $MoOCl_4$, $WOCl_4$, and $WOBr_4$ (Figure 2, Table 2) show a good correlation with the gas-phase bands [Figure 2 (*c*)—(*e*)] and the positions of the bands predicted for charge transfer (X→M) using optical electronegativities (Table 3). The set of bands for $MoOCl_4$ in a N_2 matrix at 12 K also shows reasonable agreement with those obtained previously for the compound in a CCl_4 solution,[17] and hence confirms that isolated $MoOCl_4$ molecules occur in CCl_4 solution. This solvent shifts the lowest-energy band to higher wavenumbers and may cause band broadening so that matrix bands observed at 36 630 and 31 250 cm^{-1} appear as a single band at 37 200 cm^{-1} for CCl_4 solution. With the exception of the band of $WOCl_4$ at 38 870 cm^{-1} and possibly the band * of $MoOCl_4$, at 15 500 cm^{-1}, the lack of vibrational fine structure on the bands prevents definitive assignments. However, an assignment of the bands should be possible using the ordering of energy levels in Figure 3 and the resulting transitions.[15,16] Surprisingly, the SCF-$X\alpha$-SW calculations predict the first pure O→M charge-transfer band to occur at >50 000 cm^{-1} (from 2e and 3a_1) while the lowest-energy band which *might* involve orbitals with some oxygen p character (3e and 4a_1) is assigned at *ca.* 22 000 cm^{-1} for $MoOCl_4$ ($3e \rightarrow 2b_2$) [15] and *ca.* 28 000 cm^{-1} for $WOCl_4$ ($3e \rightarrow 2b_2$).[15] The large number of bands predicted in the gas-phase studies and their assignment in clusters to broad bands is dis-

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* The doublet splitting could be a vibrational progression (Table 2) or could arise from two new degenerate transitions or spin–orbit coupling.

appointingly uninformative. On the basis of optical electronegativities, the lowest-energy O→M charge-transfer bands are tentatively assigned at 31 250 cm^{-1} for $MoOCl_4$ (31 000 ± 2 000 cm^{-1}, calculated), 37 040 cm^{-1} for $WOCl_4$ (38 000 ± 2 000, calculated), and 37 880 cm^{-1} for $WOBr_4$ (38 000 ± 2 000, calculated). Some confidence in the optical electronegativity approach can be drawn from the close agreement[37] of the lowest-energy absorption bands of $[MOX_4]^-$ ions, *e.g.* $[MoOCl_4]^-$ [27 000 (calculated) and 26 000—26 700 cm^{-1} (observed)], $[MoOBr_4]^-$ [19 000 (calculated) and 20 600 cm^{-1} (observed)], and $[WOBr_4]^-$ [24 000 (calculated) and 24 700 cm^{-1} (observed)]. A firm assignment of the band of $WOCl_4$ at 38 870 cm^{-1} as a charge-transfer (Cl→W) band can be made on the basis of the vibrational progression (300 ± 70 cm^{-1}) which may be correlated with the ground-state (E) mode (260 cm^{-1}), or alternatively, with the A_1 ν(W–Cl) vibrational mode (400 cm^{-1}). All other assignments (Table 2) must be tentative. Considering the large number of X→M charge-transfer bands it is perhaps not surprising that excitation does not lead to luminescence.

Conclusions.—The i.r. spectra of the matrix-isolated monomer MOX_4 species show no detectable amounts of decomposition products or polymers. The literature assignments of the vibrational fundamentals of these monomers have been generally confirmed and certain details clarified. High-resolution i.r. spectra, utilizing the isotopic fine structure, have been used to probe matrix site effects, and it has been shown that whilst argon often produces two trapping sites, nitrogen produces one site of rather low symmetry.

The electronic spectra of the matrix-isolated MOX_4 in nitrogen have been recorded, the results being superior to gas-phase spectra in terms of resolution, greater ease of observation of vibrational fine structure, and most importantly when taken in *parallel* with the i.r. studies, the absence of any doubts about the presence of decomposition products. A comparison of the experimental data with the results of recent $X\alpha$ calculations shows that, although these in principle give information about the number and relative energies of the orbitals, the numerical agreement is poor, and the much simpler concept of optical electronegativity provides a better estimate of the energies of the lowest O→M and X→M charge-transfer bands.

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