Infrared and Electronic Spectra of Matrix Isolated Chalcogenide Halides of Tungsten(VI), WYX_4 (Y = S or Se; X = F, Cl, or Br)

Peter J. Jones, William Levason, J. Steven Ogden,* and Jeremy W. Turff
Department of Chemistry, The University, Southampton SO9 5NH
Elizabeth M. Page and David A. Rice*
Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD

Characteristic i.r. fundamentals have been observed for the six tungsten thio- and seleno-tetrahalides WSF_4, $WSeF_4$, $WSCl_4$, $WSeCl_4$, $WSBr_4$, and $WSeBr_4$, isolated as monomers in nitrogen matrices. The electronic spectra of these species have similarly been recorded, and the principal features assigned on the basis of vibrational fine-structure. The results are compared with data previously obtained for the tungsten oxotetrahalides.

Although several chalcogenide (S, Se, or Te) halides of the transition metals have been reported in recent years,[1,2] these compounds have received much less attention than the analogous oxide halides. In the case of tunsten(VI), six thio- and seleno-tetrahalides have been prepared, *viz.* WSF_4,[3] $WSeF_4$,[4] $WSCl_4$,[5] $WSeCl_4$,[5] $WSBr_4$,[5,6] and $WSeBr_4$.[5] Single-crystal *X*-ray studies [7] of $WSCl_4$ and $WSBr_4$ have shown the presence of square-pyramidal molecules, weakly associated into dimers *via* asymmetric halide bridges, and since the $WYCl_4$ and $WYBr_4$ pairs (Y = S or Se) are isomorphous, it is probable that the selenohalides have similar structures.[5] In contrast, the oxo-species WOX_4 (X = Cl or Br) are oxygen-bridged polymers.[8] WOF_4 is a fluorine-bridged tetramer,[9] and it has been suggested that the sulphur and selenium analogues are similar.[3,4]

Data on the vapour species are much less complete, although by analogy with the oxohalides, all six chalcogen halides would be expected to be five-co-ordinate (C_{4v}) monomers. This suggestion is confirmed by recent electron diffraction data on WSF_4,[10] $WSCl_4$,[11] and $WSeCl_4$,[11] whilst mass spectrometric data [3,4,12,13] show no evidence for polymeric species. There are no published vibrational data on the vapour species, and only for $WSCl_4$ vapour has an attempt been made to study the electronic spectrum.[14]

This paper describes a matrix isolation i.r. and u.v.–visible study on the title compounds. We have recently shown that this technique yields high-quality data for monomeric WOX_4 species,[15] and our principal aim here is to extend these experiments to the sulphur and selenium analogues.

Experimental

Samples of $WSCl_4$, $WSeCl_4$, $WSBr_4$, and $WSeBr_4$ were prepared as previously described,[5,6] and were handled in all-glass systems using break-seal techniques.

The compound WSF_4 [3] was made by reacting a two-fold excess of WF_6 with Sb_2S_3 (*ca.* 2 mmol) in a Monel bomb (300 cm^3) heated to *ca.* 300 °C for *ca.* 16 h. After cooling to room temperature, the excess WF_6 was removed and the reactor opened in a nitrogen dry-box (H_2O, O_2 <10 p.p.m.). A yellow solid was removed which was identified as WSF_4 by ^{19}F n.m.r. spectroscopy using MeCN as solvent (δ −85.0 p.p.m., lit.,[3] −85.1 p.p.m., relative to $CFCl_3$). $WSeF_4$ was prepared in a similar way by heating WF_6 with Sb_2Se_3 for *ca.* 60 h at 350 °C. The ^{19}F n.m.r. spectrum of the orange product gave δ −88.2 p.p.m. (lit.[4] −87.9 p.p.m.) in MeCN.

The general features of the matrix isolation equipment have been described elsewhere,[15] and the only significant change appropriate to these experiments was the use of an all-metal spray-on system for the fluorides. Sublimation temperatures of *ca.* 40 °C were used for both i.r. and u.v.–visible studies on the two fluorides, *ca.* 70 °C for the chlorides, and *ca.* 350 °C for the bromides. Both nitrogen and argon were employed as matrix gases, but nitrogen consistently gave the better spectral quality. Electronic spectra were recorded on a PE 554 instrument.

Results and Discussion

Infrared Spectroscopy.—The i.r. frequencies obtained for the title compounds, isolated in nitrogen matrices, are summarised in Table 1, whilst Figure 1 shows typical survey spectra in which features denoted (*) arise from WOX_4 impurities.

Electron diffraction studies [10,11] have revealed square-pyramidal structures (C_{4v}) for WSF_4, $WSCl_4$, and $WSeCl_4$, and our spectral assignment assumes this structure for all six species. The vibration frequencies assigned to the tungsten–halogen stretching modes are very similar to those previously observed for the monomeric oxohalides,[15] and the terminal W=S stretches (at *ca.* 570 cm^{-1}) are identified unambiguously for all three compounds by ^{34}S satellites (*ca.* 4% abundance) lying *ca.* 14 cm^{-1} below the principal $W{=}^{32}S$ peak (Table 1). The calculated $^{32}S \longrightarrow {}^{34}S$ frequency shift for an uncoupled W=S unit vibrating at 570 cm^{-1} is 14.5 cm^{-1}.

One disappointing feature of these spectra, however, was our failure to locate the terminal W=Se modes with equal confidence. Our $WSeCl_4$ spectra [*e.g.* Figure 1(*d*)] showed no evidence of this band in the frequency ranges 200—360 and 400—1 000 cm^{-1}, and we believe it is probable that it is obscured by the more intense W–Cl modes lying between 360 and 400 cm^{-1}. In $WSeF_4$ and $WSeBr_4$, however, where this spectral region is clear of halogen modes, we observe only very weak features at 380 cm^{-1} ($WSeF_4$) and 368 cm^{-1} ($WSeBr_4$). These bands were only observed in thick deposits, and as a selenium isotope pattern could not be resolved, their assignment remains tentative.

Previous i.r. studies on these compounds have been carried out on the solids, primarily as an aid to structural identification, and it is interesting to compare our monomer frequencies with this work. Solid WSF_4[3] shows terminal W–F modes at 699, 673, and 643 cm^{-1} and features at 534 and 514 cm^{-1} which are assigned as W–F bridge modes. The position of ν(W=S) in the solid lies at the same frequency (577 cm^{-1}) as in our monomer spectrum, and there is little doubt that the fluorine-bridged polymer model proposed for the solid is correct. The i.r. spectra of solid $WSCl_4$ and $WSBr_4$ similarly show terminal modes ν(W=S) which correspond very closely to our monomer values.

For the solid selenohalides, however, there appears to be less consistency. The i.r. spectrum of solid $WSeF_4$ shows

Table 1. Vibration frequencies (cm^{-1}) and assignments for WYX_4 species isolated in nitrogen matrices (Y = O, S, or Se; X = F, Cl, or Br)

WOF_4 [a]	WSF_4	$WSeF_4$	$WOCl_4$ [a]	$WSCl_4$	$WSeCl_4$	$WOBr_4$ [a]	$WSBr_4$	$WSeBr_4$	Mode
1 058	577	380 (?)	1 032	568	—	1 025	564	368 (?)	$\nu_{W-Y}(A_1)$
726	707	702	400	397	399	—	—	—	$\nu_{W-X}(A_1)$
686	671	669	380 [b]	372 [b]	369 [b]	264	250	247	$\nu_{W-X}(E)$

	Sulphur isotope effects		
Mode	WSF_4	$WSCl_4$	$WSBr_4$
$\nu(W={}^{32}S)$	577.3	567.6	564.0
$\nu(W={}^{34}S)$	562.9	553.5	550.0
$\Delta\nu$	14.4	14.1	14.0

[a] Ref. 15. [b] Centre of complex absorption.

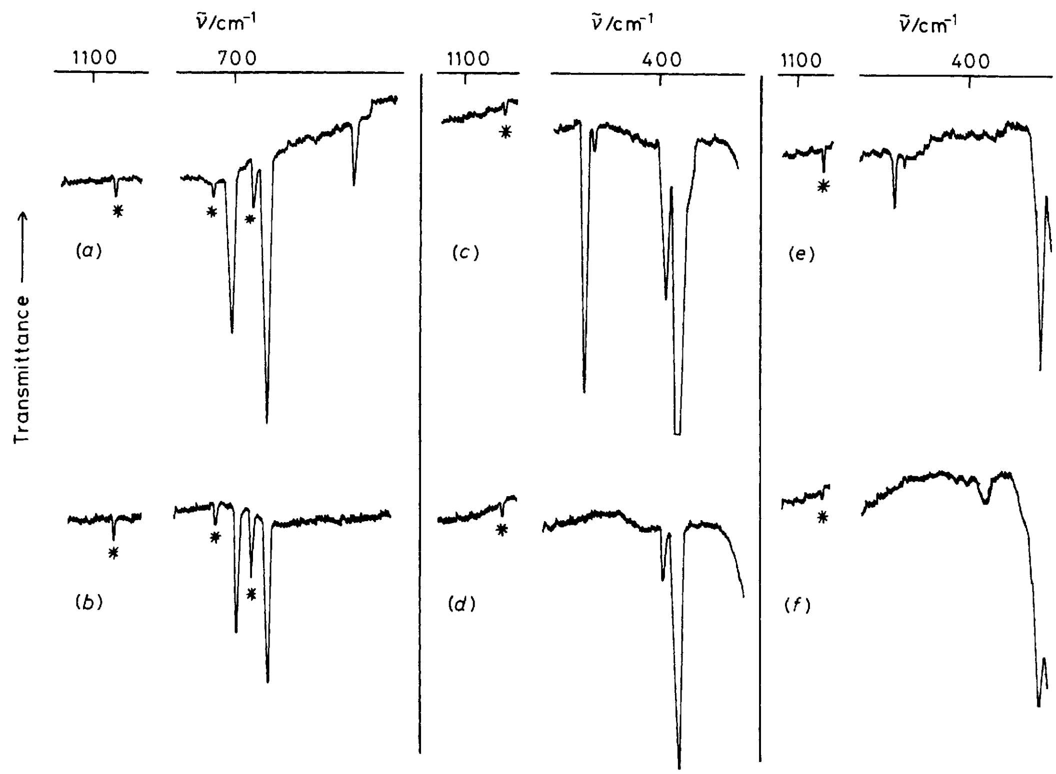

Figure 1. Nitrogen matrix i.r. spectra obtained for (*a*) WSF_4, (*b*) $WSeF_4$, (*c*) $WSCl_4$, (*d*) $WSeCl_4$, (*e*) $WSBr_4$, and (*f*) $WSeBr_4$. Features denoted (*) arise from WOX_4 impurity

features assigned to terminal and bridging W–F modes, but also a strong band at 366 cm^{-1} which is assigned as ν(W=Se).[4] Although our solid samples also showed this feature, our matrix spectra yielded only a weak band at 380 cm^{-1}. In contrast, the corresponding W=Se mode could not be located in solid $WSeBr_4$,[5] and appeared only weakly in our matrix experiments at 368 cm^{-1}. In solid $WSeCl_4$ features at 388 [11] or 396 cm^{-1} [6] have been identified as ν(W=Se).

The principal conclusion arising from these experiments, however, is that spectroscopic data on the monomer species are readily obtained using matrix isolation techniques, and that the level of impurity is relatively low.

Electronic Spectroscopy.—Samples for u.v.–visible studies were checked for purity by carrying out an i.r. matrix study immediately prior to deposition, and in some cases, a further i.r. spectrum was recorded *after* the electronic spectrum. In this way, it may be confidently assumed that the u.v.–visible absorptions recorded are those of the species identified in the i.r., and the presence of specific impurities such as the oxo-halides, which have well characterised i.r. bands, may be established.

The subsequent assignment of u.v.–visible spectra may be approached in two ways: *via* optical electronegativities,[16] or with the aid of SCF–Xα–SW molecular orbital (m.o.) calculations. Such calculations have been performed for $WSCl_4$,[14] and although extension to $WSBr_4$ and $WSeX_4$ would be difficult owing to the presence of heavier atoms, some correlation of energy levels might be anticipated. The optical electronegativity approach predicts only the lowest energy ligand →metal charge-transfer (c.t.) band but has been helpful in the earlier interpretation [15] of the electronic spectra of matrix isolated WOX_4 (X = F, Cl, or Br). Since, in general, no allowance is made in this model for the effect of other ligands (L′) upon specific L ⟶ M c.t. energies, it would be predicted that the lowest X ⟶ W c.t. bands in WOX_4, WSX_4, and

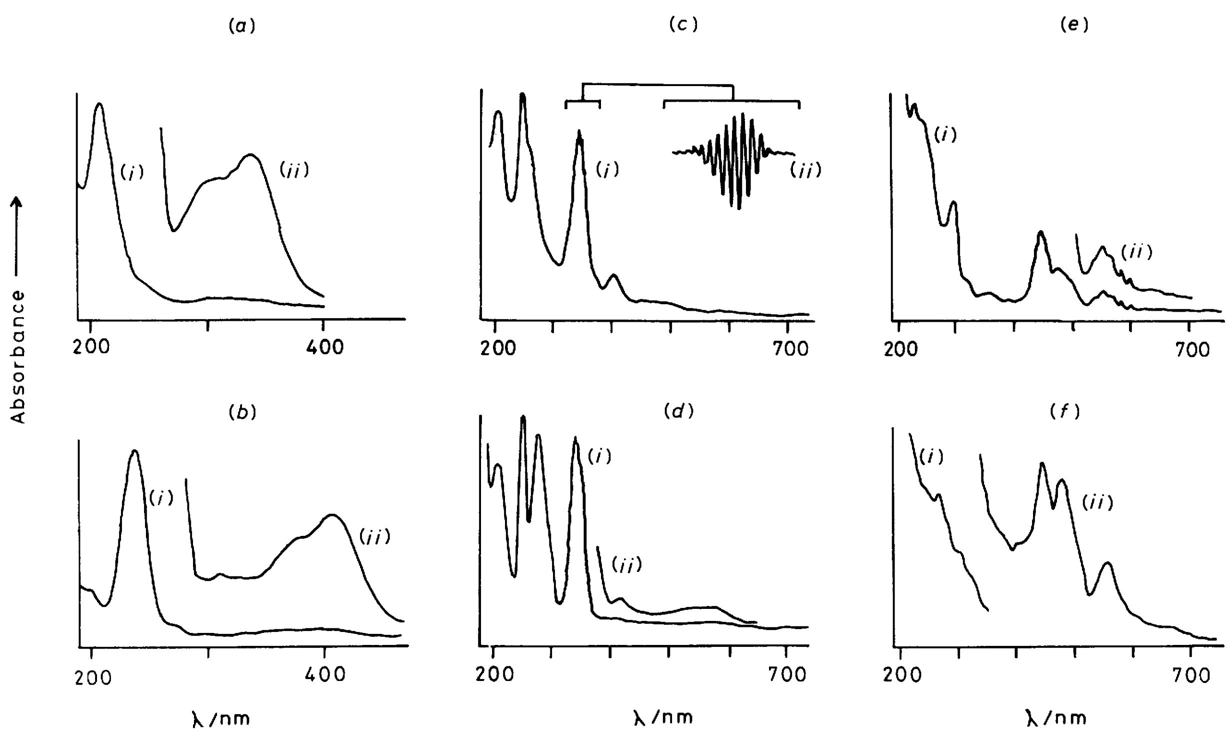

Figure 2. Nitrogen matrix u.v.–visible spectra (*i*) obtained for (*a*) WSF_4, (*b*) $WSeF_4$, (*c*) $WSCl_4$, (*d*) $WSeCl_4$, (*e*) $WSBr_4$, and (*f*) $WSeBr_4$. For (*a*), (*b*), (*d*), (*e*), and (*f*) spectra (*ii*) were recorded after extended deposition. Spectrum (*c*)(*ii*) shows typical vibrational fine-structure observed using derivative recording

$WSeX_4$ would all have similar positions. On the basis of our earlier studies, these would therefore be expected at *ca.* 39 000 (F), *ca.* 22 000 (Cl), and *ca.* 15 000 cm^{-1} (Br). The major problem is to estimate realistic values of the optical electronegativities ($\chi_{opt.}$) for S and Se in order to predict the position of the S ⟶ W and Se ⟶ W c.t. bands. Values for $\chi_{opt.}$(S) and $\chi_{opt.}$(Se) of 2.4 and 2.2 have been obtained [16] from studies on $[WS_4]^{2-}$ and $[WSe_4]^{2-}$, but it was suggested that tetrahedral species might not be a reliable source of these parameters when used predictively in five- or six-fold co-ordination. In particular, it has been found that $\chi_{opt.}$(O) is significantly lower for $[WO_4]^{2-}$ than in the WOX_4 molecules previously studied [15] and values for $\chi_{opt.}$(S) and $\chi_{opt.}$(Se) suitable for this present series of molecules may well lie in the ranges 2.7—2.9 and 2.6—2.8 respectively. Such uncertainty inevitably makes assignments of S ⟶ W and Se ⟶ W c.t. bands on this basis alone unsatisfactory, but these values do indicate that the relevant c.t. bands will lie below those expected for F ⟶ W [$\chi_{opt.}$(F) = 3.9] and Cl ⟶ W [$\chi_{opt.}$(Cl) = 3.0] but of similar energy to Br ⟶ W c.t. bands [$\chi_{opt.}$(Br) = 2.8].

Fortunately, however, many of the u.v.–visible absorptions observed in these experiments showed vibrational fine-structure which could be correlated with ground state A_1 stretching modes, and derivative spectroscopy proved invaluable in extracting this information. Typical survey spectra obtained for all six WYX_4 species isolated in nitrogen matrices are shown in Figure 2, whilst Table 2 summarises the band positions and proposed assignments.

WSF_4 *and* $WSeF_4$. These compounds were handled in an all-metal system, and the i.r. spectra show that contamination by WOF_4 is small. The principal feature in the electronic spectrum of each compound is a intense high-energy absorption, and this lies at 47 845 cm^{-1} for WSF_4 [Figure 2(*a*)] and at 42 195 cm^{-1} for $WSeF_4$ [Figure 2(*b*)]. In WOF_4, the lowest energy F ⟶ W c.t. band has been assigned [15] at 39 500 cm^{-1}. The high-energy bands in WSF_4 and $WSeF_4$ are therefore similarly assigned. After extended deposition, both compounds show several very much weaker features at lower energy. In WSF_4, the most prominent band maximum lies at 32 680 cm^{-1} and this is accompanied by a vibrational progression of *ca.* 450 cm^{-1}.

In the ground electronic state of this molecule, ν(W=S) lies at 577 cm^{-1} and we therefore assign the feature at 32 680 cm^{-1}, and the other longer wavelength bands, to S ⟶ W c.t. It was not possible to resolve vibrational fine-structure for the corresponding $WSeF_4$ absorptions, but the parallel assignment of Se ⟶ W c.t. seems reasonable.

$WSCl_4$ *and* $WSeCl_4$. The u.v.–visible spectra of the chlorides [Figure 2(*c*) and (*d*)] were found to be much richer in absorptions, but a comparison between these results and those for $WOCl_4$, together with the observation of vibrational structure on several bands, provides an almost complete assignment. Firstly we note that the four bands at 49 260, 40 160, 28 985, and 24 390 cm^{-1} in $WSCl_4$ have similar positions and relative intensities to features at 48 075, 39 680, 29 155, and 24 040 cm^{-1} in $WSeCl_4$. In addition, it is found that the vibrational spacing of *ca.* 345 cm^{-1} on the $WSCl_4$ band at 28 985 cm^{-1} is virtually identical to that found (*ca.* 345 cm^{-1}) on the 29 155 cm^{-1} band of $WSeCl_4$. Both molecules have ground state A_1(W–Cl) stretching modes at *ca.* 400 cm^{-1} (Table 1) and these bands are therefore assigned as Cl ⟶ W c.t. transitions.

The $WSCl_4$ spectrum also shows features at 38 315 and 21 010 cm^{-1} which would appear to have counterparts at 35 840 and 17 700 cm^{-1} in $WSeCl_4$. The change in absorption positions suggests their assignment to be S ⟶ W or Se ⟶ W c.t., and this is supported by vibrational fine-structure. In particular, the band at 38 315 cm^{-1} in $WSCl_4$ shows a progression of *ca.* 455 cm^{-1}, whilst a value of *ca.* 425 cm^{-1} is obtained for the absorption at 21 010 cm^{-1}. These compare very favourably with the progression of *ca.* 450 cm^{-1} found in

Table 2. Electronic spectra of matrix isolated WSX_4 and $WSeX_4$

Complex	Band maxima [a] (nm)	(cm^{-1})	Vibrational fine-structure [b] (cm^{-1})	Assignment [c]
WSF_4	209	47 845	—	F → W
	247	40 485	—	F → W
	306	32 680	450	S → W
	337	29 675	—	S → W
$WSeF_4$	237	42 195	—	F → W
	269	37 175	—	F → W
	306	32 680	—	Se → W
	376	26 595	—	Se → W
	406	24 630	—	Se → W
$WSCl_4$	203	49 260	—	Cl → W
	249	40 160	—	Cl → W
	261	38 315	455	S → W
	345	28 985	345	Cl → W
	410	24 390	—	Cl → W
	476	21 010	425	S → W
$WSeCl_4$	208	48 075	—	Cl → W
	230	43 480	—	Cl → W
	252	39 680	—	Cl → W
	279	35 840	—	Se → W
	343	29 155	345	Cl → W
	416	24 040	—	Cl → W
	ca. 565	*ca.* 17 700	285	Se → W
$WSBr_4$	231	43 290	—	—
	247	40 485	—	—
	259	38 610	—	S → W
	298	33 560	—	Br → W
	320	31 250	—	—
	361	27 700		Br → W
	448	22 320	220	Br → W
	478	20 920	210	Br → W [d]
	556	17 985	*ca.* 450	S → W [e]
	ca. 650	*ca.* 15 385	—	Br → W
$WSeBr_4$	225	44 445	—	—
	240	41 670	—	—
	264	37 880	—	Se → W
	300	33 355	—	Br → W
	325	30 770	255	Se → W
	360	27 780	—	Br → W
	403	24 815	—	—
	443	22 575	210	Br → W
	477	20 965	220	Br → W [f]
	560	17 860	—	*g*
	665	15 040	265	Se → W

[a] Spectra measured in wavelength. [b] Average vibrational spacing (± *ca.* 50 cm^{-1}). [c] Assignments tentative in the absence of vibrational fine-structure, see text. [d] Composite of $WSBr_4$ absorption at *ca.* 500 nm and $WOBr_4$ band at 480 nm. [e] Composite of $WSBr_4$ absorption at *ca.* 570 nm and $WOBr_4$ band at 561 nm. [f] Composite of $WSeBr_4$ absorption at *ca.* 500 nm and $WOBr_4$ band at 480 nm. [g] Appears to mainly be due to $WOBr_4$ impurity.

WSF_4. The $WSeCl_4$ band at 17 700 cm^{-1} shows a partially resolved progression of *ca.* 280 cm^{-1}.

The $WSCl_4$ assignments proposed here may also be examined in the light of SCF–Xα–SW calculations by Topol *et al.*[14] A schematic m.o. diagram based upon this work is shown in Figure 3, and in contrast with that for $WOCl_4$,[15] it is concluded that S contributes to several of the higher filled orbitals. One would therefore expect transitions involving S → W character to occur at significantly lower energies. In particular, the lowest allowed absorption, $5e \rightarrow 2b_2$, originates from an orbital with a large amount of sulphur character, and would correspond to the band at 21 010 cm^{-1}. Similar considerations indicate that the features at 24 390 and 28 985 cm^{-1} be assigned as $4e \rightarrow 2b_2$ and $1a_2 \rightarrow 6e$.

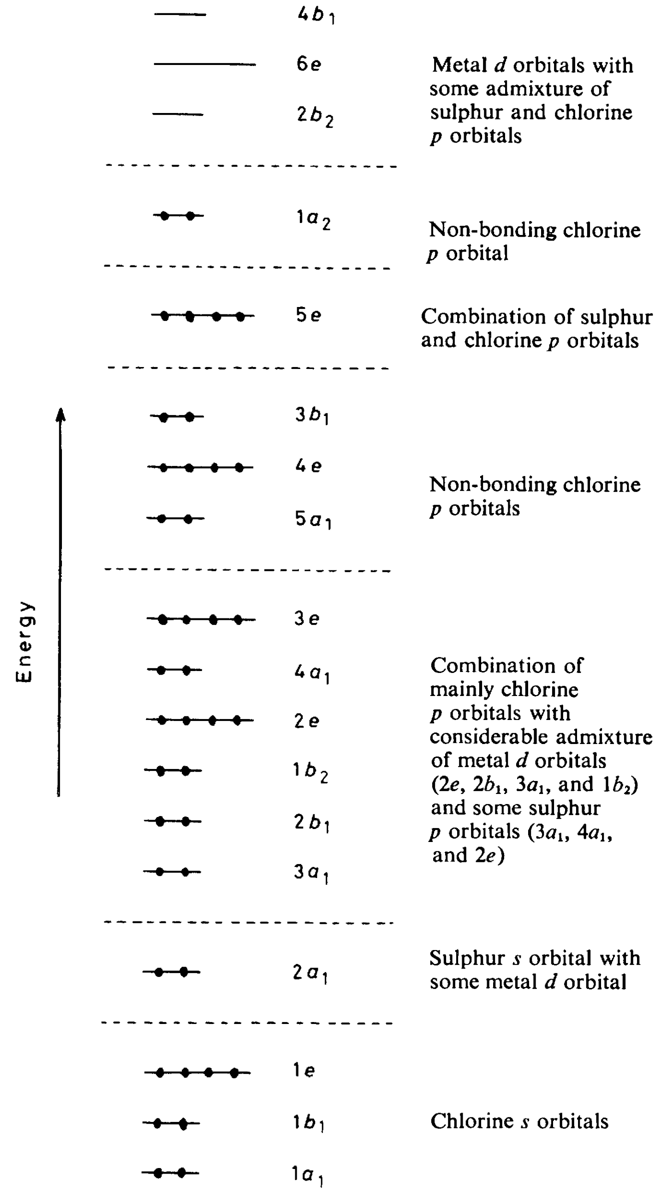

Figure 3. Schematic m.o. diagram for $WSCl_4$ based on data from ref. 14

$WSBr_4$ *and* $WSeBr_4$. As noted earlier, the i.r. spectra of these compounds always showed the presence of some $WOBr_4$, and this impurity was also evident from the electronic spectra. Some bands showed variable relative intensity between experiments, whilst others exhibited distorted vibrational progressions. In particular, the bands at 20 920 and 17 985 cm^{-1} in $WSBr_4$ were rather unsymmetrical and could well be overlapped by $WOBr_4$ features known [15] to lie at 20 830 and 17 830 cm^{-1}. However, the absorption at 17 985 cm^{-1} showed a progression of *ca.* 450 cm^{-1} indicating at least a substantial component from $WSBr_4$.

Similar criteria concerning the spectra of $WSeBr_4$ indicate that the band at 20 965 cm^{-1} might involve some contribution from $WOBr_4$, whilst the band at 17 860 cm^{-1} is perhaps principally $WOBr_4$. Apart from these uncertainties, the assignments of the remaining bands follow by analogy with the chlorides. The lowest energy Se $\longrightarrow$ W and Br $\longrightarrow$ W transitions are both expected at *ca.* 15 000 cm^{-1}, and our feature at 15 040 cm^{-1} is assigned as Se $\longrightarrow$ W c.t. rather than Br $\longrightarrow$ W c.t. by virtue of the magnitude of the vibrational spacing.

Conclusions

The i.r. spectra described here are all consistent with the isolation of C_{4v} monomeric species, and require no further discussion. However, our tabulation of the corresponding electronic spectra raises two points. The optical electronegativity approach predicts that the lowest energy S $\longrightarrow$ W c.t. transition should occur at the same frequency irrespective of halogen, and that a similar situation should exist for the Se $\longrightarrow$ W transition in the selenohalides. This expectation appears to hold approximately from our assignment of the lowest energy *observed* bands in the chlorides and bromides, but it is evident from Table 2 that the lowest observed maxima for the fluorides are significantly higher in energy (*e.g.* 29 675 cm^{-1} in WSF_4 compared with 21 010 and 17 985 cm^{-1} in $WSCl_4$ and $WSBr_4$ respectively). This could be interpreted as a significant breakdown in the model.

However, Figure 2 shows that the absorption tails in WSF_4 and $WSeF_4$ extend by at least 5 000 cm^{-1} to low energy, and it is quite possible that the lowest S $\longrightarrow$ W and Se $\longrightarrow$ W c.t. transitions are present as weak *unresolved* absorptions. Nevertheless, there would still appear to be a trend to lower energies for these S $\longrightarrow$ W and Se $\longrightarrow$ W transitions as a function of halogen such that F > Cl > Br, and the schematic m.o. diagram for these compounds (Figure 3) provides one possible explanation. As a result of the relatively low symmetry of these molecules, the c.t. transitions responsible for these absorptions involve orbitals comprising both chalcogen and halogen character. Some breakdown of the 'separability' approximation is therefore inevitable, and there is evidence from elsewhere [15] that fluorides might be expected to show the most significant departures.

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