Spectroscopic Studies on Matrix Isolated Osmium Pentafluoride Oxide, Osmium Tetrafluoride Oxide, and Osmium Difluoride Trioxide†

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The title compounds $OsOF_5$, $OsOF_4$, and OsO_3F_2 have been isolated as monomeric species in inert-gas matrices at low temperatures, and studied by i.r. and u.v.–visible spectroscopy. In particular, the electronic spectra of these three molecules are described for the first time, and the principal charge-transfer bands assigned. The i.r. spectrum of molecular $OsOF_4$ is also reported for the first time, and shows prominent absorptions at *ca.* 1 079 (Os=O) and *ca.* 685 cm^{-1} (Os–F) consistent with C_{4v} geometry.

Four oxide fluorides of osmium are currently known: OsO_3F_2, OsO_2F_3, $OsOF_5$, and $OsOF_4$,[1–4] and there is some evidence for the existence of OsO_2F_2.[5] These compounds are all highly reactive, and previous spectroscopic studies have largely been confined to the solid phases. However, mass spectrometric studies indicate that these compounds can all exist as monomer species in the vapour phase,[3] and our interest lies primarily in the characterisation of these molecules using a combination of matrix isolation and i.r. and u.v.–visible techniques. The advantages offered by this approach lie first in the stabilisation of the highly reactive monomers, and secondly in the relatively narrow linewidths and cumulative sampling procedure which usually ensures spectra of sufficient quality to permit an unequivocal assignment. Recent examples of related compounds studied in this way include $CrOF_4$[6] and $OsOCl_4$.[7]

There are no reports of the electronic spectra of any of the title compounds. Vibrational data have been obtained for molecular OsO_3F_2 (i.r. and Raman of matrix-isolated species)[4] and for $OsOF_5$ (i.r. and Raman of vapour)[8] but not for monomeric $OsOF_4$. The strategy adopted in these experiments has therefore been to use mass spectrometry and matrix i.r. spectroscopy to establish the conditions most suitable for isolating monomeric species, and subsequently to carry out u.v.–visible studies.

Experimental

Sample Preparation.—The preparation of pure samples in the Os/O/F system is not easy, and may be further complicated, as regards the vapour species, by disproportionation and dismutation reactions.[3] In our hands, the reported preparations of $OsOF_5$ *via* $OsO_2 + F_2$[2] or $Os + O_2 + F_2$[8] gave appreciable amounts of OsF_6 as an impurity. However the reaction between OsF_6 and OsO_4 was found to yield reproducible samples of $OsOF_4$ and $OsOF_5$ depending upon conditions, and typical syntheses are outlined below.

$OsOF_4$. OsO_4 (0.2 g, 0.8 mmol) was loaded into a 300-cm^3 Monel autoclave together with an excess of OsF_6 (*ca.* 2 mmol) and the mixture heated to 423 K for 16 h. At the end of this period, the autoclave was cooled to room temperature, and the excess OsF_6 and other volatiles removed *in vacuo*. The autoclave was then opened in a dry-box (< 5 p.p.m. H_2O), and yellow-green $OsOF_4$ scraped from the surface and stored in stainless steel containers.

$OsOF_5$. OsO_4 (0.4 g, 1.6 mmol) and OsF_6 (1 g, 3.2 mmol) were similarly loaded into the autoclave and heated for *ca.* 20 h at the somewhat higher temperature of 473 K. The autoclave was then cooled to *ca.* 250 K prior to the removal of volatiles, and then warmed to 273 K. At this temperature, the autoclave was transferred to the dry-box, and on opening was found to contain blue-green $OsOF_5$, which was similarly stored in stainless steel containers.

OsO_3F_2. Samples of OsO_3F_2 were prepared in good yield by the method of Sunder and Stevie.[3] In a typical synthesis, OsO_4 (1 g, 4 mmol) was loaded into the Monel autoclave in a dry-box, and the autoclave filled with F_2 to 1 atm. The main body of the autoclave was then heated to *ca.* 570 K for 16 h whilst cooling the lid with an efficient flow of water. After cooling to room temperature, the volatiles were pumped out (mainly excess F_2) and the autoclave was opened in the dry-box. Orange-yellow crystals of OsO_3F_2 were scraped off the lid and stored in stainless steel containers.

Sample Purity.—The three title compounds are *very* sensitive to moisture, and despite minimal handling in pre-fluorinated apparatus, our spectra routinely showed OsO_4 as a persistent impurity in all systems. Positive identification of specific oxide fluorides was therefore based on mass spectrometric or matrix i.r. identification linked to previously established volatilities. In addition, it was necessary to carry out supporting matrix experiments on OsO_4 to eliminate absorptions due to this molecule. This presented no problems in the i.r., where transitions were typically single, sharp absorptions, but difficulties were initially encountered in the u.v.–visible studies owing to the extent and complexity of the vibrational structure on each electronic transition, and to the fact that OsO_4 has very intense charge-transfer (c.t.) bands. Quite modest impurity levels thus result in u.v.–visible spectra dominated by OsO_4 transitions. This problem could only satisfactorily be overcome by spectral subtraction.

Techniques.—The general features of our matrix-isolation i.r. and u.v.–visible equipment have been described elsewhere.[9] In this present work, samples of OsO_3F_2 and $OsOF_4$ were loaded into pre-fluorinated stainless steel containers and pumped for several hours at $< 10^{-6}$ Torr to remove as much OsO_4 as possible. Samples were then vaporised by raising the temperature to *ca.* 360 or 400 K respectively. The more volatile $OsOF_5$ was vaporised directly from the Monel autoclave maintained at *ca.* 258—263 K. Nitrogen or argon (BOC 99.999%) were used as matrix gases, and samples were deposited onto an optically transparent window cooled to *ca.* 12 K. I.r. studies were carried out using PE225 and 983G spectrometers and CsI optics. U.v.–visible studies employed LiF optics and a PE554 spectrometer which was interfaced with a microcomputer, thus permitting spectral averaging and subtraction.

Mass spectrometric studies were carried out on $OsOF_4$ and

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† *Non-S.I. units employed:* atm = 101 325 Pa, Torr = 101 325/760 Pa.

$OsOF_5$ using a VG SXP400 quadrupole instrument fitted with a cross-axis molecular beam sampling system. Vaporisation temperatures in these experiments were generally slightly higher (by *ca.* 10 K) than those employed in the corresponding matrix depositions.

Results

I.r. and Mass Spectroscopy.—$OsOF_5$. I.r. and Raman spectra of vapour phase $OsOF_5$ have been reported by Holloway *et al.*,[8] and their results are interpreted on the basis of a C_{4v} monomer. In particular, prominent i.r. absorptions were assigned at 964 [ν(Os=O), A_1], *ca.* 717 [ν(Os–F), A_1], *ca.* 700 [ν(Os–F), E], *ca.* 645 [ν(Os–F), A_1], and *ca.* 280 cm^{-1} [δ(OsF_4), A_1]. The previously reported[3] mass spectrum of this compound was recorded at a sample temperature of 298 K, and showed ion peaks which included $OsOF_4^+$, $OsOF_3^+$, and a relatively weak parent ion $OsOF_5^+$.

Our samples of $OsOF_5$ were maintained at *ca.* 270 K for mass spectrometric studies, and gave a similar distribution of ions, together with signals due to OsO_4^+ and OsO_3^+ which decayed with time. Corresponding matrix-isolation studies showed prominent i.r. absorptions at 966.5, 712.0, 694.5, 635.0, and 282.0 cm^{-1} in argon, with counterparts at 966.5, 713.0, 695.0, 638.5, and 284.5 cm^{-1} in nitrogen [Figure 1(*a*)]. Both matrices therefore gave spectra in good agreement with the gas-phase data, and this comparison is summarised in Table 1.

However, two additional absorptions were also routinely observed in these matrix experiments. These occurred at 1 078.5 and 956.0 cm^{-1} in argon (1 079.5 and 960.5 cm^{-1} in nitrogen) and their growth patterns did not correlate with the $OsOF_5$ absorptions. The band at 956.0 cm^{-1} was relatively more prominent in the initial stages of sample deposition, whilst the 1 078.5 cm^{-1} feature could be enhanced, at the *expense* of increased growth of $OsOF_5$ bands, by warming the spray-on tube during deposition. This latter band is therefore provisionally assigned as a decomposition product of $OsOF_5$. The band at 956.0 cm^{-1} is identified as the T_2 stretching mode of OsO_4 by reference to our mass spectrometric results and by comparison with earlier work.[4] The growth of this impurity in the initial stages of sample deposition indicates that it is produced by hydrolysis in those parts of the spray-on line close to the cryostat which cannot be adequately passivated.

Table 1. Prominent i.r. bands (cm^{-1}) observed in matrix-isolation studies on osmium oxide fluorides

	This work[a]			
	N_2 matrix	Ar matrix	Previous work	Assignments
$OsOF_5$	966.5	966.5	964[b]	ν_1 (A_1)
(C_{4v})	713.0	712.0	717[b]	ν_2 (A_1)
	638.5	635.0	645[b]	ν_3 (A_1)
	284.5	282.0	280[b]	ν_4 (A_1)
	695.0	694.5	700[b]	ν_8 (E)
OsO_3F_2	641.0	646.0	646.0[c]	ν_3 (A_2'')
(D_{3h})	931.0	928.0	928.0[c]	ν_5 (E')
$OsOF_4$	1 079.5	1 078.5		ν_1 (A_1)
(C_{4v})	685.0	682.5		ν_7 (E)
	319.0	318.0		ν_8 (E)
(OsO_4)	960.5	956.0	956.0[c]	ν_3 (T_2)
(T_d)	330.0	326.5	327.0[c]	ν_4 (T_2)

[a] Frequency accuracy ±1 cm^{-1}. [b] Gas phase: ref. 8. [c] Argon matrix: ref. 4.

OsO_3F_2. Previous matrix-isolation studies on OsO_3F_2[4] have established that this molecule has D_{3h} symmetry, and the principal i.r. absorptions in argon matrices are assigned as 928.0 [ν(Os=O), E'] and 646.0 cm^{-1} [ν(Os–F), A_2'']. This earlier work also showed that despite repeated sublimations, it proved impossible to obtain spectra completely free from OsO_4 impurity. In the present experiments, the initial matrix i.r. spectra similarly showed the characteristic OsO_4 absorption at *ca.* 956 cm^{-1} (argon) and this was gradually overtaken in intensity by the OsO_3F_2 modes at 928 and 646 cm^{-1} as deposition continued. In nitrogen matrices, these latter absorptions appeared at *ca.* 931 and *ca.* 641 cm^{-1}, and a typical spectrum from this system is shown in Figure 1(*b*).

$OsOF_4$. There are no previous vibrational data for monomeric $OsOF_4$, but the mass spectrum of this material heated to 323 K shows[10] a low intensity ion $OsOF_4^+$, and an electron diffraction study[11] has been interpreted on the basis of a C_{4v} monomer geometry. This structure is known to be adopted by many MOX_4 species in the vapour phase,[12–14] and characteristic metal–oxygen and metal–halogen modes have been assigned for the monomers in low-temperature matrices.[7,15] In particular, ν(Os=O) (A_1) lies at *ca.* 1 030 cm^{-1} in $OsOCl_4$,[7] and intense W=O and W–F stretching modes have been noted at *ca.* 1 055 and 690 cm^{-1} respectively[15] in WOF_4.

In the present studies, samples of $OsOF_4$ were vaporised at a temperature of *ca.* 400 K, and the mass spectrum of the vapour showed prominent ions corresponding to $OsOF_4^+$, $OsOF_3^+$,

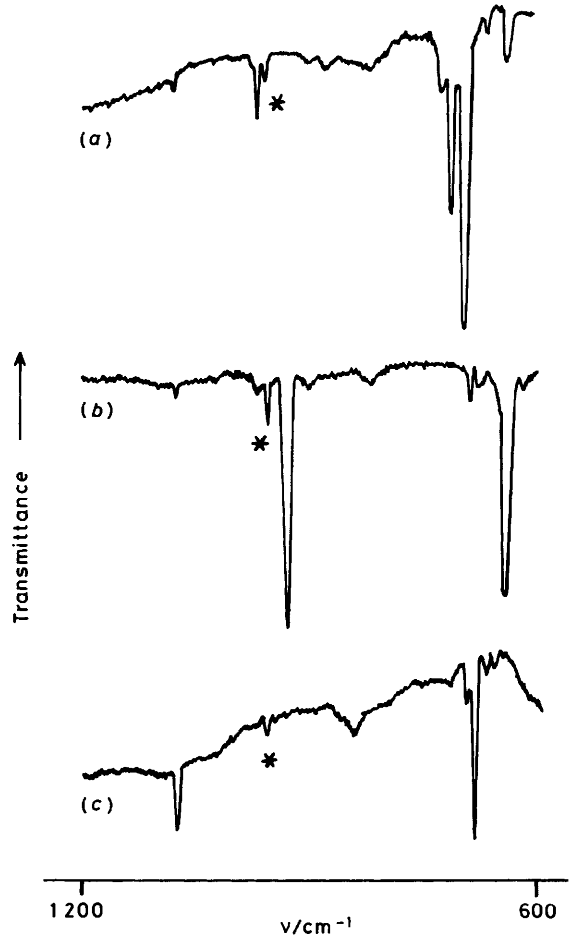

Figure 1. Nitrogen matrix i.r. spectra (1 200—600 cm^{-1}) obtained from samples of (*a*) $OsOF_5$, (*b*) OsO_3F_2, and (*c*) $OsOF_4$. The OsO_4 impurity band (*ca.* 960 cm^{-1}) is denoted (*)

OsO_4^+, and OsO_3^+. Nitrogen matrix spectra obtained under similar vaporisation conditions showed new bands at 1 079.5 and 685.0 cm^{-1} in addition to the T_2 stretch of OsO_4, and a typical spectrum is shown in Figure 1(*c*). By analogy with the related MOX_4 species,[15] these two new bands are assigned as ν(Os=O) (A_1) and ν(Os–F) (E) in C_{4v} $OsOF_4$. An associated weak bending mode was observed at *ca.* 318 cm^{-1} and a weak shoulder at *ca.* 695 cm^{-1} is tentatively assigned to ν(Os–F) (A_1).

Finally, these experiments provide an assignment for the second impurity band previously noted in the $OsOF_5$ system. As indicated earlier, when $OsOF_5$ vapour is deposited *via* a heated (*ca.* 350 K) tube, an additional spectral feature is observed to grow in at *ca.* 1 079 cm^{-1}. We therefore believe that under these conditions, $OsOF_5$ is decomposing in the vapour phase to yield monomeric $OsOF_4$. This explanation is supported by closer examination of the Os–F stretching region, where we observed the corresponding growth of the $OsOF_4$ absorption at *ca.* 685 cm^{-1} during $OsOF_5$ deposition.

U.v.–Visible Spectra.—The electronic spectra of monomeric $OsOF_5$, $OsOF_4$, and OsO_3F_2 isolated in nitrogen matrices at 12 K were recorded over the range 190—850 nm (*ca.* 52 000—12 000 cm^{-1}). Typical spectra are shown in Figures 2—4, and the band positions are listed in Table 2, together with comparative data for $OsOCl_4$.[7]

As indicated earlier, OsO_4 was present as a persistent impurity in all matrix experiments. In the u.v. region, this compound exhibits two intense and highly structured absorptions and these complicated our attempts to obtain oxide fluoride spectra. Fortunately, in the $OsOF_5$ experiments, OsO_4 contamination only occurred in the initial stages, and it was therefore possible to obtain good spectra of $OsOF_5$ by confining sample deposition on the central window to the later stages of the experiment. However spectra from $OsOF_4$ and

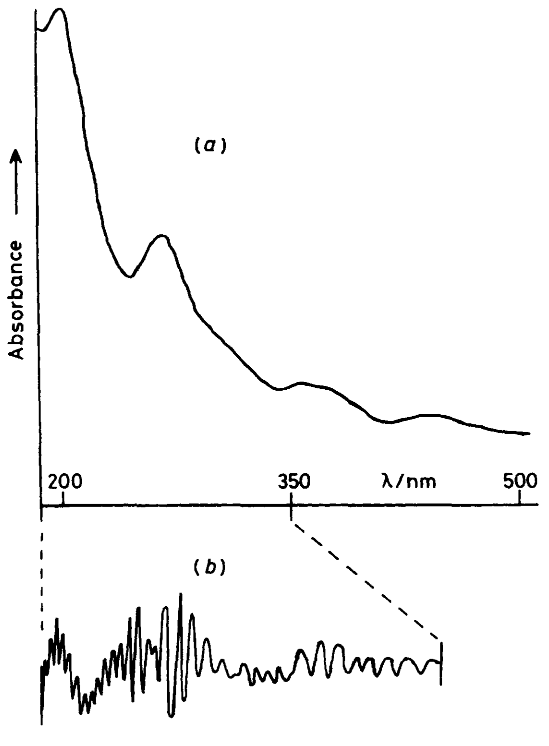

Figure 2. Nitrogen matrix u.v.–visible spectra (190—500 nm) obtained from $OsOF_5$. (*a*) Principal absorptions under low resolution, (*b*) second derivative spectrum under higher resolution showing vibrational progressions between 190 and 350 nm

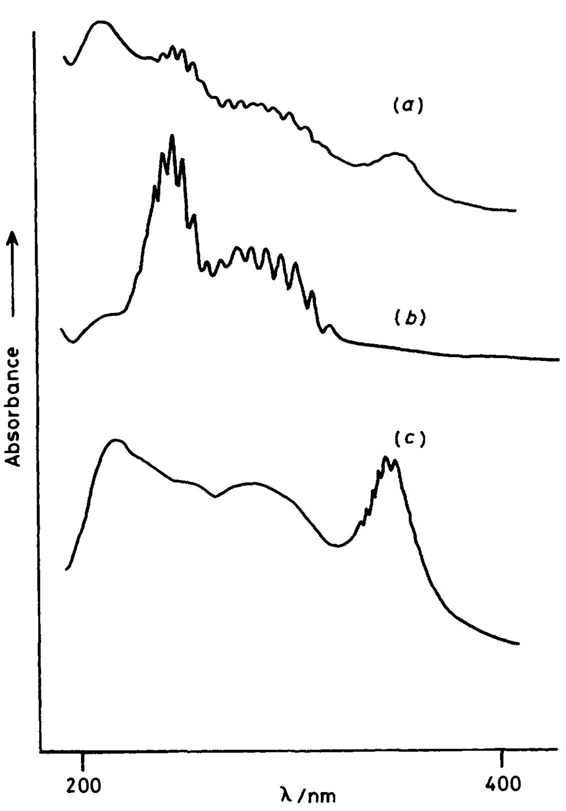

Figure 3. Nitrogen matrix u.v.–visible spectra (200—400 nm) obtained from OsO_3F_2 and OsO_4. (*a*) Typical spectrum obtained from OsO_3F_2 vaporised at *ca.* 360 K. (*b*) Spectrum obtained from OsO_4. (*c*) Spectrum (*a*) under higher resolution with OsO_4 absorptions subtracted out

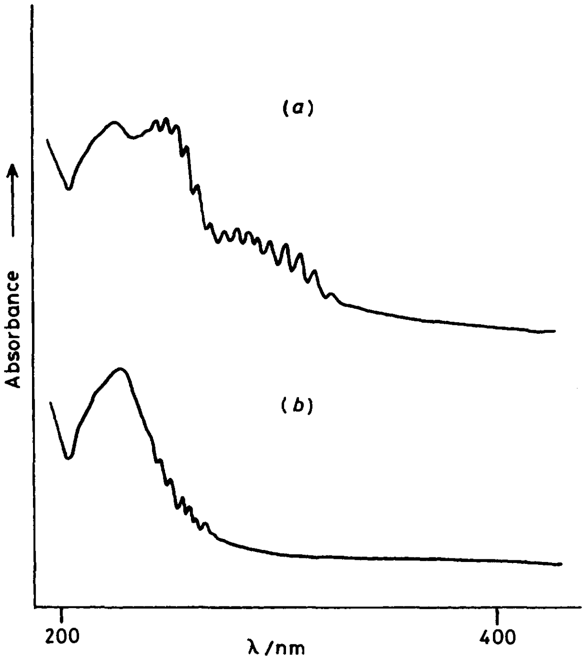

Figure 4. (*a*) Nitrogen matrix u.v.–visible spectrum (200—400 nm) obtained from $OsOF_4$ at *ca.* 400 K. (*b*) Spectrum obtained after removal of OsO_4 absorptions

Table 2. U.v.–visible spectra of osmium oxide halides isolated in low-temperature nitrogen matrices

	$E_{max.}$/cm^{-1} [a]	Vibrational spacing (cm^{-1})	Assignment
$OsOF_5$	48 500	*ca.* 620	F ⟶ Os c.t.
	37 000	*ca.* 840	O ⟶ Os c.t.
	31 750 (sh)	*ca.* 690	F ⟶ Os c.t.
	27 500	—	O ⟶ Os c.t. (?)
	22 600vw	—	*d–d*
	21 300vw	—	*d–d*
OsO_3F_2	46 500	—	—
	43 400 (sh)	—	—
	35 300	—	F ⟶ Os c.t.
	28 800	*ca.* 820	O ⟶ Os c.t.
$OsOF_4$ [b]	46 700	—	F ⟶ Os c.t.
	41 700 (sh)	*ca.* 940	O ⟶ Os c.t.
	16 600vw	—	*d–d*
$OsOCl_4$ [c,d]	44 445	—	—
	39 215 (sh)	—	O ⟶ Os c.t.
	29 155	—	Cl ⟶ Os c.t.
	25 905	—	Cl ⟶ Os c.t.
	21 700vw	—	*d–d*
	20 500vw	—	*d–d*

[a] Accuracy ±50 cm^{-1}. [b] For comparison, WOF_4 has F ⟶ W c.t. at 39 560 and a weaker shoulder at *ca.* 38 000 cm^{-1}. [c] Data from ref. 7. [d] For comparison, $WOCl_4$ has prominent bands at 44 840, 38 870, 37 040, 28 270, and 26 320 cm^{-1}.

OsO_3F_2 samples showed that small, but varying, amounts of OsO_4 were codepositing continuously *throughout* each experiment, and spectral subtraction (with different weightings) was necessary to remove the OsO_4 absorptions.

Although subtraction of complex band envelopes is subject to some error, we are confident that in this case the procedure is not producing artefacts. This is because our difference spectra show excellent reproducibility over a large number of experiments, in which varying proportions of OsO_4 impurity are present.

Interpretation of the u.v.–visible spectra of metal oxide halides can be attempted *via* molecular orbital (m.o.) calculations (*e.g.* SCF-Xα-SW calculations) or in a more limited way *via* the optical electronegativity model which affords predictions of the *lowest* energy X, O ⟶ M transitions. No m.o. calculations for the osmium oxide fluorides have been performed, and hence the latter approach will be used. Jørgensen[16] has estimated χ_{opt} (Os^{VI}) as 2.6 and by extrapolation $\chi_{opt}(Os^{VII})$ and $\chi_{opt}(Os^{VIII})$ will be *ca.* 2.7—2.9. For F^-, χ_{opt} = 3.9 but establishment of a value for O^{2-} is difficult[16] since as a result of the $M_{d\pi}$–$O_{p\pi}$ interactions χ_{opt}(O) varies both with M, and with the number of oxide ligands. Values of *ca.* 3.5—3.2 have been suggested for different systems resulting in a spread of *ca.* 9 000 cm^{-1} in the predicted values of the O ⟶ M c.t. transitions.

$OsOF_5$. Osmium(VII) has the [Xe] $5d^1$ configuration and in C_{4v} symmetry the *d*-orbital ordering expected is d_{xy} (b_2) < d_{xz}, d_{yz} (e) < $d_{x^2-y^2}$ (b_1) < d_{z^2} (a_1) with the ground state d_{xy}.[1] The only other Os^{VII} species for which a u.v.–visible spectrum has been reported[17] is the ion $[OsO_4]^-$ which has O ⟶ Os charge-transfer bands at > *ca.* 33 000 cm^{-1}. The optical electronegativity formula predicts for $OsOF_5$ F ⟶ Os at 33 000—36 000 cm^{-1} and (less certainly) O ⟶ Os at 21 000—24 000 cm^{-1} (±3 000 cm^{-1}), both uncorrected for spin pairing. The spectrum of the matrix-isolated molecule (Figure 2) shows intense absorptions at 48 500, 37 000 cm^{-1}, a distinct shoulder at 31 750 cm^{-1} and a broad feature centred at 27 500 cm^{-1}. Vibrational progressions of *ca.* 620, 840, and 690 cm^{-1} (±70 cm^{-1}) were observed respectively on the three higher energy bands. The 840 cm^{-1} progression correlates with the ground state A_1 ν(Os=O) at *ca.* 965 cm^{-1} and leads to an O ⟶ Os c.t. assignment for the band at 37 000 cm^{-1}. The possibility that this progression is due to OsO_4 [A_1 ν(Os=O) *ca.* 960 cm^{-1}] was ruled out both by the absence of the second strong band of the OsO_4 spectrum [Figure 3(*b*)], and by the constant relative intensities of the main spectral features of $OsOF_5$ over several experiments, indicative of a single species. The progressions of *ca.* 620 and 690 cm^{-1} correlate with the two A_1 ν(Os–F) vibrations at *ca.* 640 and *ca.* 715 cm^{-1} and indicate F ⟶ Os c.t. assignments for the bands at 48 500 and 31 750 cm^{-1}. The feature at *ca.* 27 500 cm^{-1} shows no progression, but seems likely to be an O ⟶ Os c.t. transition. Two very much weaker features at 22 600 and 21 300 cm^{-1} appeared after prolonged deposition, and may be *d–d* transitions. The spectrum of *solid* $OsOF_5$ deposited on a cold window in the absence of matrix gas was essentially the same as that of the matrix-isolated material.

OsO_3F_2. The i.r. and Raman spectra of matrix isolated OsO_3F_2 show the monomer to have a trigonal-bipyramidal structure (D_{3h}).[4] For this geometry the *d*-orbital ordering is predicted to be d_{xz}, d_{yz} (e'') < $d_{x^2-y^2}$, d_{xy} (e') < d_{z^2} (a_1). All i.r. and u.v.–visible spectra of OsO_3F_2 in nitrogen or argon matrices showed OsO_4 to be also present. A typical experimental spectrum and the result of spectral subtraction of the OsO_4 are shown in Figure 3(*a*) and (*c*) respectively. The only other osmium(VIII) compounds for which u.v.–visible spectra have been described are OsO_4 [Figure 3(*b*)], and the six-coordinate species $[OsO_3F_3]^-$ (C_{3v}) and $[OsO_4F_2]^{2-}$ (C_{2v}).[18] The spectra of these anions show rising absorptions at > *ca.* 22 000 cm^{-1} with rather ill-defined maxima at *ca.* 27 700, 35 700, and 41 000 cm^{-1}.

The spectrum of OsO_3F_2 [Figure 3(*c*)] shows four bands in the 27 000—48 000 cm^{-1} region, but unfortunately only the lowest (28 800 cm^{-1}) shows any resolved fine structure. The latter corresponds to a progression of 820 ± 20 cm^{-1} which correlates with the Raman active A_1 ν(Os=O) at *ca.* 950 cm^{-1},[4] and identifies this as an O ⟶ Os c.t. transition. Definitive assignments of the remaining three are not possible, but it seems likely on the basis of optical electronegativities, and by comparison with $OsOF_5$ that the band at 35 300 cm^{-1} is F ⟶ Os. The optical electronegativity concept predicts that $\chi_{opt}(Os^{VIII}) > \chi_{opt}(Os^{VII})$, and therefore that the lowest energy F ⟶ Os and O ⟶ Os c.t. bands should be at lower energy in OsO_3F_2 than $OsOF_5$. In practice, the reverse is observed (Table 2) and whilst it is always possible that weak band(s) to low energy may not be resolved from the tails of more intense bands, it is more likely that this reversal reflects the effect of the three oxygen atoms in OsO_3F_2 interacting strongly with e''(d_{xz}, d_{yz}) $Os_{d\pi}$–$O_{p\pi}$ and thus raising the energy of the metal acceptor orbitals.

$OsOF_4$. Figure 4(*a*) shows a typical u.v.–visible spectrum obtained from the vaporisation of $OsOF_4$. The well resolved structure is characteristic of OsO_4 [Figure 3(*b*)], and after subtraction of the latter, Figure 4(*b*) was obtained, which we believe to be the spectrum of $OsOF_4$ monomer.

Its assignment, however, is not straightforward. The optical electronegativity model predicts the lowest O, F ⟶ Os c.t. bands at slightly higher frequencies than for $OsOF_5$, but since d^2(C_{4v}) $OsOF_4$ will have the ground-state configuration $d_{xy}{}^2$, the lowest possible c.t. transitions are to d_{yz}, d_{xz}, and the predicted energies must be increased by the d_{xy}–d_{yz}, d_{xz} separation. For $OsOCl_4$ it has been proposed[7] that the latter separation may be *ca.* 15 000—20 000 cm^{-1}, and an O ⟶ Os transition was assigned at 39 215 cm^{-1}. Hence for $OsOF_4$ one would expect O ——→ Os at similar energy and F ——→ Os somewhat higher. A comparison between the u.v.–visible transitions in $OsOCl_4$ and $WOCl_4$ is also instructive (Table 2). Here it is noticeable that the major transitions in the spectra of $OsOCl_4$ and $WOCl_4$ are similar in both profile *and energy*. This is because the shifts to lower energy expected on passing from W to Os are almost cancelled out by the filling of the lowest *d* orbital in osmium(VI). The energies of the transitions are thus increased by an amount equal to the d_{xy}–d_{xz}, d_{yz} separation. Hence $OsOF_4$ should resemble WOF_4 for which a F ——→ W transition has been observed[15] at 39 560 cm^{-1}. The O ——→ W transition was not observed in this previous study of WOF_4 and subsequent studies of other MYX_4 species (including WSX_4,[19] $WSeX_4$,[19] and $CrOF_4$[6]) showed that Y ——→ M transitions were relatively weak compared with X ——→ M. Re-examination of WOF_4 with improved instrumentation as part of the present study failed to yield clear evidence for the O ——→ W c.t. transition, although an ill defined shoulder (*ca.* 38 000 cm^{-1}) on the low energy side of the F ——→ W transition may be the band sought. Unfortunately no vibrational structure to support this assignment was evident.

On the basis of the optical electronegativity formula and the comparisons with $OsOCl_4$ and WOF_4, we therefore assign the broad band at 46 700 cm^{-1} as F ——→ Os and the shoulder at *ca.* 41 700 cm^{-1} as O ——→ Os. The latter shows some structure which derivative recording reveals as a progression of 940 $\pm$ 40 cm^{-1}, and this is consistent with the ground state A_1 ν(Os=O) of *ca.* 1 080 cm^{-1}. After prolonged deposition a weak feature at 16 600 cm^{-1} was found, and is assigned as a *d–d* transition.

Conclusions

Matrix i.r. studies have been used to establish the conditions under which the three compounds $OsOF_5$, OsO_3F_2, and $OsOF_4$ may be isolated as monomeric species, and their principal i.r. absorptions are assigned. In particular, $OsOF_4$ has characteristic Os=O and Os–F modes at *ca.* 1 079 and *ca.* 685 cm^{-1} respectively consistent with C_{4v} geometry, and it is shown that this species is also a product of the thermal decomposition of $OsOF_5$.

The u.v.–visible spectra of all three monomers have been obtained for the first time, and although these spectra are complicated by the presence of OsO_4 impurity, they may be satisfactorily assigned using the optical electronegativity model.

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