Spectroscopic Studies on the Hexafluorides of Rhenium, Osmium, Iridium, and Platinum isolated in Low-temperature Matrices†

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The compounds ReF_6, OsF_6, IrF_6, and PtF_6 have been isolated as monomeric species in inert-gas matrices at low temperatures, and characterised by i.r. spectroscopy. Subsequent u.v.–visible studies reveal a complex pattern of electronic absorptions, and a detailed assignment of these in terms of charge transfer, *d–d*, and intra-configurational transitions is presented.

The hexafluorides of the later transition elements constitute examples of discrete molecular compounds in rare oxidation states, and as such their spectroscopic characterisation is of especial interest.

Of the known hexafluorides only XeF_6[1,2] does not have octahedral symmetry although four, those of Tc, Ru, Re, and Os, exhibit distortions of the dynamic Jahn-Teller type.[3–8] The octahedral structural information, which was obtained primarily on the basis of i.r. and Raman data, was comprehensively reviewed in 1965[9] and, since then, for many of the molecules all of the required i.r. and Raman bands have been observed directly[9,10] or have been deduced from combination bands. Electron diffraction studies on WF_6, OsF_6, IrF_6, UF_6, NpF_6, and PuF_6[11–13] and electric deflection studies on SF_6, SeF_6, TeF_6, MoF_6, WF_6, UF_6, RuF_6, RhF_6, ReF_6, OsF_6, IrF_6, and PtF_6[14] have also provided support for the octahedral arrangements in these fluorides.

The present paper describes detailed studies of the i.r. and in particular the u.v.–visible spectra of ReF_6, OsF_6, IrF_6, and PtF_6 isolated in inert-gas matrices. The matrix-isolation technique allows high resolution spectroscopic studies of these extremely reactive materials with minimal corrosion and containment problems. Previous u.v.–visible data on these hexafluorides is limited. Moffitt *et al.*[15] produced survey spectra (4 000—50 000 cm^{-1}) in the gas phase, but due to instrumental difficulties there were gaps in the range covered, and intense high energy (> 25 000 cm^{-1}) bands were not well defined, either in terms of $E_{max.}$ or relative intensities. Apart from a subsequent study of ReF_6 by McDiarmid[16] the high energy regions have not been further examined, but considerable efforts have been devoted to the study of the intra-configurational bands in the near-i.r. and visible regions, in the gas phase and in crystals, and for the MF_6 diluted in WF_6 or MoF_6 hosts at low temperatures.[17–19] Consequently, the present work will concentrate upon the high energy region.

Experimental

The hexafluorides OsF_6, IrF_6, and ReF_6 were obtained in high yield by the direct fluorination of the metals in pre-fluorinated nickel reactors fitted with stainless-steel high pressure valves (Autoclave Engineers).[14,20] The hexafluorides of osmium and iridium were prepared by heating the metal sponge (Johnson Matthey) with a 67% excess of fluorine at 300 °C and 4—5 atm pressure for 4—5 h. To ensure that no contamination with the heptafluoride occurred, rhenium hexafluoride was made by heating a 5% excess of the reduced metal sponge with 5 atm pressure of fluorine at 300 °C.

Direct fluorination of platinum in a closed system was also used for the preparation of PtF_6.[21] However, in this case, yields were less than 40%. The platinum metal sponge was combined with a large excess of fluorine ($Pt:F_2 = 1:15$) at 200 °C and 15 atm for 5 h.

The fluorides were purified by sublimation and their initial purity was monitored by vibrational spectroscopy and mass spectrometry.

All four hexafluorides were stored in pre-seasoned nickel containers fitted with Hoke bellows valves (type 4171 M2B), and, in order to ensure a controllable flux of material from these containers, they were cooled using slush baths. The general features of our matrix-isolation i.r. and u.v.–visible equipment have been described elsewhere.[22] In this present work, the samples of ReF_6, OsF_6, IrF_6, and PtF_6 were maintained at temperatures of 190, 195, 200, and 232 K respectively during deposition. Both nitrogen and argon (BOC 99.999%) were used as matrix gases, but spectral quality was generally better in nitrogen. I.r. studies were carried out using a PE 983G spectrometer, and a matrix rig fitted with CsI optics, whilst u.v.–visible experiments employed LiF optics and a PE 554 spectrometer interfaced with a microcomputer. Matrix ratios were estimated to be well in excess of 1 000:1.

Supporting mass spectrometric studies were also carried out on the title compounds using a VG SXP 400 quadrupole instrument. At sample temperatures very similar to those employed in the matrix experiments, the parent ions MF_6^+ were detectable in all cases, but the most intense signals were for the fragments MF_5^+ as has been noted previously.[23,24]

Results and Discussion

I.r. Spectroscopy.—The vibrational fundamentals of ReF_6, OsF_6, IrF_6, and PtF_6 have been reported previously,[9,10] and our main reasons for carrying out matrix-isolation i.r. studies here were, first to check sample purity, and secondly to establish suitable deposition conditions. All four hexafluorides have O_h symmetry, and each molecule is thus expected to show two i.r.-active fundamentals (T_{1u} symmetry). Our spectra in argon and nitrogen matrices showed characteristic absorptions in the regions 700—750 cm^{-1} and 200—300 cm^{-1} due to these modes. Figure 1 shows typical survey spectra obtained from the title compounds, whilst Table 1 compares our matrix frequencies with previous gas-phase data. The optimum conditions for sample deposition are detailed in the Experimental section.

Matrix spectra obtained from ReF_6, IrF_6, and PtF_6 (Figure 1) indicated that the samples were essentially free from significant impurity but, in the case of OsF_6, our i.r. spectra routinely showed the presence of OsO_4, which gives a characteristic band at *ca.* 960 cm^{-1} ($\nu_{Os=O}$, T_2). As noted elsewhere,[25] OsO_4 is a persistent impurity in osmium fluoride

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† *Non-S.I. units employed:* atm = 101 325 Pa, B.M. = 9.274×10^{-24} J T^{-1}.

Table 1. Principal i.r. absorptions (cm^{-1}) of ReF_6, OsF_6, IrF_6, and PtF_6

Compound	Gas phase[a]	N_2 matrix[b]	Ar matrix[b]	Assignment
ReF_6	715	716.4, 712.7	719.4, 714.0	$\nu_3(T_{1u}$ stretch)
	257	262.7	258.6	$\nu_4(T_{1u}$ bend)
OsF_6	720	724.9, 712.3	726.5, 712.2	ν_3
	268	266.2	273.8, 260.4	ν_4
IrF_6	719	719.1, 717.2	719.3, 716.0	ν_3
	276	279.1	283.3	ν_4
PtF_6	705	704.4	705.2	ν_3
	273	273.8	274.2	ν_4

[a] From refs. 9 and 10. [b] This work: frequency accuracy ±0.5 cm^{-1}.

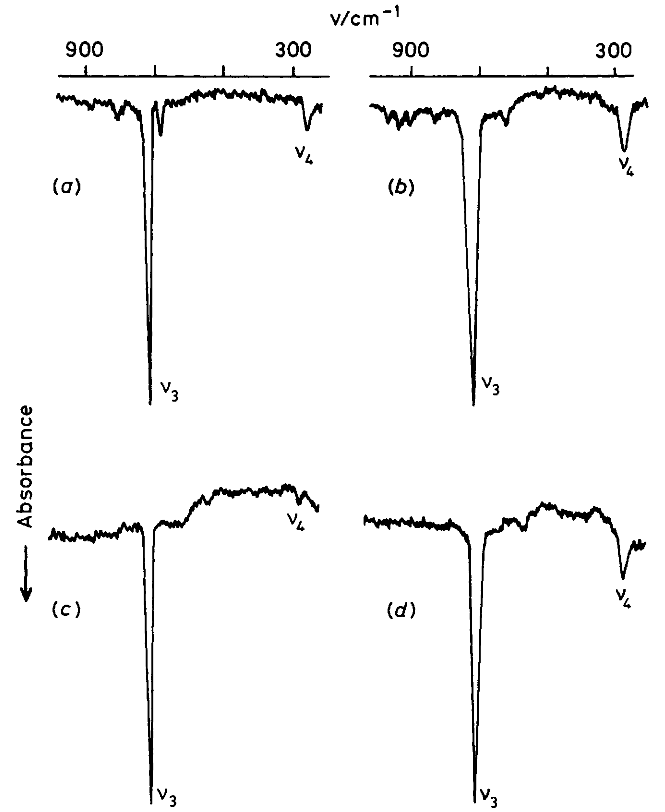

Figure 1. I.r. spectra of matrix-isolated hexafluorides: (*a*) ReF_6 in N_2, (*b*) OsF_6 in N_2, (*c*) IrF_6 in N_2, (*d*) PtF_6 in Ar

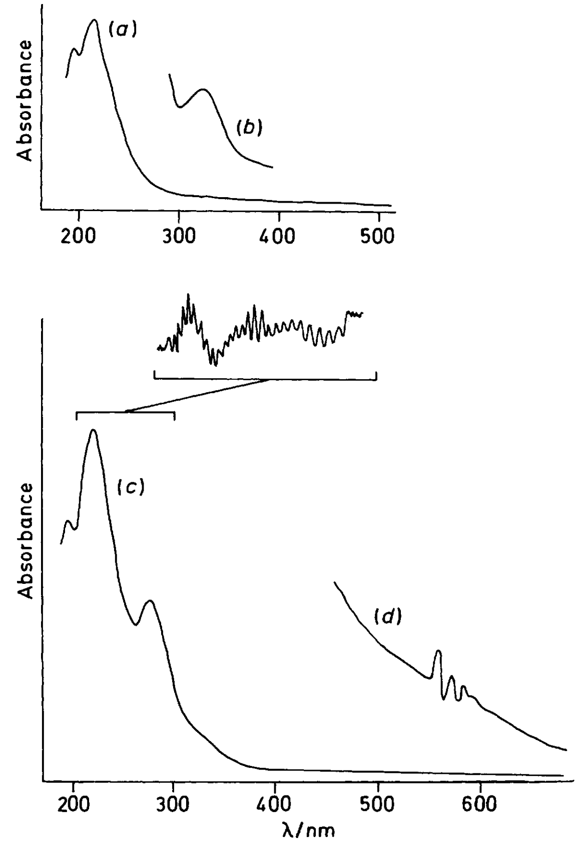

Figure 2. U.v.–visible spectra of matrix isolated ReF_6 and OsF_6: (*a*) ReF_6 in N_2, (*b*) ReF_6 in N_2 after prolonged deposition, (*c*) OsF_6 in N_2 (inset: 200—300 nm region with derivative recording), (*d*) OsF_6 in N_2 after prolonged deposition

chemistry, and in these experiments, it almost certainly arises from hydrolysis in those parts of the spray-on system which cannot be adequately seasoned. Its presence presents no problems in the interpretation of the i.r. spectrum but, unless determined steps are taken to prevent its formation, even small amounts are likely to complicate subsequent u.v.–visible studies.[26] Fortunately, as deposition proceeds, the growth of this impurity diminishes, and its formation may be virtually eliminated by passing OsF_6 through the spray-on system prior to cool-down.

Examination of the T_{1u} stretching modes under higher resolution revealed band splittings for all four hexafluorides which were generally too large to be accounted for simply by metal isotope effects. Thus for OsF_6 in nitrogen, two components were observed at 724.9 and 712.3 cm^{-1} with an approximate intensity ratio 1 : 2, whilst IrF_6 in argon showed an almost equal doublet at 719.3, 716.0 cm^{-1}. In the former case, the splitting may be due to a lifting of the T_{1u} degeneracy,* but for IrF_6 in Ar and some of the other systems studied, multiple trapping sites seem to offer the most probable explanation. The principal components observed for each species are included in Table 1.

These i.r. studies established the conditions under which the title compounds could be satisfactorily isolated in low-temperature matrices. They were generally carried out

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* The origin of these splittings could lie in static Jahn-Teller distortions (see, for example, B. Weinstock H. H. Claassen, and J. Malm, *J. Chem. Phys.*, 1960, **32**, 181), but splittings of similar magnitude may also arise as a result of matrix perturbations (see, for example, E. G. Hope, W. Levason, J. S. Ogden, M. Tajik, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1985, 529).

Table 2. U.v.–visible spectra of WF_6, ReF_6, OsF_6, IrF_6, and PtF_6

	$E_{\text{max.}}/\text{cm}^{-1}$ and $(\Delta\nu/\text{cm}^{-1})$[a]		
Compound	Previous work[b]	This work[c]	Assignment
WF_6	66 711[d]		$\pi(F) \rightarrow t_{2g}(W)$
	63 127[d]		$\pi(F) \rightarrow t_{2g}(W)$
	58 350[d]		$\pi(F) \rightarrow t_{2g}(W)$
ReF_6	56 404(700)[e]		$\pi(F) \rightarrow t_{2g}(Re)$
	49 322(660)[e]	50 700	$\pi(F) \rightarrow t_{2g}(Re)$
	47 687[e]	46 800	$\pi(F) \rightarrow t_{2g}(Re)$
	32 500	30 190	${}^2T_{2g}(\Gamma_8) \rightarrow {}^2E_g(\Gamma_8)$
	5 000		${}^2T_{2g}(\Gamma_8) \rightarrow {}^2T_{2g}(\Gamma_7)$
OsF_6		> 51 000	$\pi(F) \rightarrow t_{2g}(Os)$
		45 435(630)	$\pi(F) \rightarrow t_{2g}(Os)$
	40 800		See text
		36 230(660)	$\pi(F) \rightarrow t_{2g}(Os)$
	35 700		See text
	17 300	17 340	${}^3T_{1g}(\Gamma_3) \rightarrow {}^1A_{1g}$
	8 500		${}^3T_{1g}(\Gamma_3) \rightarrow {}^1T_{2g}, {}^1E_g$
	4 300		${}^3T_{1g}(\Gamma_3) \rightarrow {}^3T_{1g}(\Gamma_4, \Gamma_1)$
	3 930		Hot band (?)
IrF_6	42 000	43 400(650)	$\pi(F) \rightarrow t_{2g}(Ir)$
	35 500	35 700(650)	$\pi(F) \rightarrow t_{2g}(Ir)$
	28 200(sh)	30 400(sh)	$\pi(F) \rightarrow t_{2g}(Ir)$
	16 000	16 000	${}^4A_{2g}(\Gamma_8) \rightarrow {}^2T_{2g}(\Gamma_8)$
	13 000	13 000	${}^4A_{2g}(\Gamma_8) \rightarrow {}^2T_{2g}(\Gamma_7)$
	9 000		${}^4A_{2g}(\Gamma_8) \rightarrow {}^2T_{1g}(\Gamma_6, \Gamma_8)$
	6 400		${}^4A_{2g}(\Gamma_8) \rightarrow {}^2E_g(\Gamma_8)$
PtF_6	45 500	46 500(sh)	$\sigma(F) \rightarrow t_{2g}(Pt)$
	32 000	32 895(560)	$\pi(F) \rightarrow t_{2g}(Pt)$
		26 250(560)	$\pi(F) \rightarrow t_{2g}(Pt)$
	25 000	23 500(555)	$\pi(F) \rightarrow t_{2g}(Pt)$
	16 000	16 000	${}^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}$
	12 000	12 000	${}^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}, {}^1E_g$
	5 400		${}^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3)$
	5 200		${}^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_5)$
	3 300		${}^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_4)$

[a] Vibrational spacings accurate to $\pm 50\ \text{cm}^{-1}$. [b] Data taken from ref. 15 unless otherwise stated. [c] N_2 matrices 11 000—52 000 cm^{-1} range. [d] Data taken from ref. 32. [e] Data taken from ref. 16.

immediately prior to the u.v.–visible experiments, and in many cases also immediately afterwards in order to check the integrity of the sample.

U.v.–Visible Spectra.—Electronic spectra were recorded over the range *ca.* 190—900 nm (52 000—11 000 cm^{-1}) for the title compounds isolated in nitrogen matrices at 12 K. Several u.v.–visible experiments were performed on each compound, and reproducibility between runs was excellent. In order to record the complete spectrum, deposits were examined at various stages during deposition, and the very intense bands in the u.v. were detectable after a relatively short spray-on time (*ca.* 10 min). Considerably thicker deposits were needed to observe the sharp, weak bands at low energy, but it was not possible to measure absolute values for the absorption coefficients of any of the bands.

Many of the more intense bands showed extensive vibrational structure which could be satisfactorily resolved using second derivative recording, and examples of typical spectra from ReF_6, OsF_6, IrF_6, and PtF_6 are shown in Figures 2 and 3. Table 2 compares our matrix data and assignments with previous work on these systems.

Three types of electronic transition are expected for these molecules: intra-configurational bands arising from a redistribution of electrons within the spin-orbit split t_{2g} levels; *d–d* transitions between the t_{2g} and e_g levels; and charge-transfer (c.t.) transitions F (π or σ) $\longrightarrow$ M(t_{2g} or e_g). Theoretical treatment of the spectra of 5*d* elements is difficult, since the large spin-orbit couplings mean that relativistic effects must be explicitly considered in addition to ligand-field components. Moffitt *et al.*[15] treated the intermediate coupling situation using the $t_{2g}{}^n$–p^{6-n} formalism and the *j–j* coupling scheme, whilst Allen and Warren[27] used the strong field O* double group approach. Our assignments of the intra-configurational bands, which typically appear as weak, sharp, features at low energy, are based on this latter model.

The charge-transfer bands may in principle be assigned *via* a molecular orbital approach.[28,29] However, although recent calculations using a non-relativistic overlapping sphere $X\alpha$ multiple scattering method have provided realistic estimates for the ionisation potentials and electron affinities of the 5*d* hexafluorides, the predictions[29] of charge-transfer transition energies are in poor agreement with experiment. Some improvement in such calculations is anticipated following better experimental data but for the present, our interpretation of the charge-transfer bands is necessarily based on an earlier model.

Jørgensen[30] has proposed that the charge-transfer bands in many hexahalide species may be rationalised in terms of the expression; $\pi(X) \longrightarrow t_{2g}(M) = V + KD + q(A - E)$, where A and D are related to the corresponding Racah parameters, E represents the variation in orbital energy with occupation number (q), and V and K are parameters dependent upon the metal (primarily oxidation state and atomic number) and ligand. The application of this model to MF_6 and $MF_6{}^{n-}$

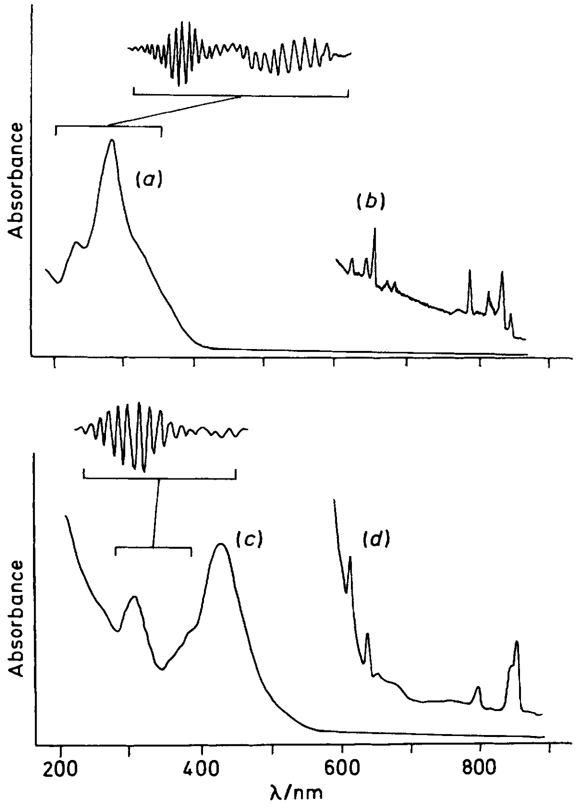

Figure 3. U.v.–visible spectra of matrix isolated IrF_6 and PtF_6: (*a*) IrF_6 in N_2 (inset: 200—350 nm region with derivative recording), (*b*) IrF_6 in N_2 after prolonged deposition, (*c*) PtF_6 in N_6 (inset: 280—380 nm region with derivative recording), (*d*) PtF_6 in N_2 after prolonged deposition

spectra has been discussed in detail by Allen and Warren.[27] A second approach is to use the optical electronegativity concept,[31] which can be expressed as $\pi(X) \rightarrow t_{2g}(M) = 30\,000\,[\chi_{\text{opt.}}(F^-) - \chi_{\text{opt.}}(M^{6+})]$. Corrections may be made for both spin-pairing and relativistic effects but, since the $\chi_{\text{opt}}(M^{6+})$ values in the literature have been derived from the hexafluorides, this approach is inappropriate here. Indeed, it would seem desirable to use our data to check and perhaps refine the values of $\chi_{\text{opt.}}(M^{6+})$ for possible use in other systems.

The u.v.–visible results reported here, together with earlier data on WF_6, form a d^0—d^4 spectral sequence, and it is convenient to discuss each hexafluoride in turn.

WF_6. The electronic spectrum of WF_6 contains no intra-configurational or *d–d* bands, and in the gas phase,[32] the lowest energy absorption lies at 58 350 cm^{-1}. For O_h MF_6 species, the ligand π orbitals transform as $t_{1g} + t_{2g} + t_{1u} + t_{2u}$. These lie to higher energy than the σ set $(a_{1g} + e_g + t_{1u})$ and the observed absorption is assigned as a $\pi(F) \rightarrow t_{2g}(W)$ c.t. transition.

ReF_6. For the d^1 species ReF_6 (μ = 0.25 B.M.), Moffitt *et al.*[15] assigned a weak band at *ca.* 5 000 cm^{-1} as the intra-configurational transition ${}^2T_{2g}(\Gamma_8) \rightarrow {}^2T_{2g}(\Gamma_7)$, and observed a shoulder at *ca.* 32 500 cm^{-1} on the rising high-energy absorption. McDiarmid[16] reported bands at 47 687, 49 322, and 56 404 cm^{-1}, assigning the first as $\pi(F) \longrightarrow$ Re c.t. and the others as members of a Rydberg series. She did not report any band at *ca.* 30 000 cm^{-1}. Subsequently, all three of McDiarmid's bands were reassigned[32] as $\pi(F) \rightarrow t_{2g}(Re)$ c.t. transitions.

Our spectra [Figure 2(*a*)] show a band at 46 800 cm^{-1}, a second intense band at *ca.* 50 700 cm^{-1} just below instrument cut-off, and a weak feature at 30 190 cm^{-1}. This lowest energy band was estimated to be approximately two orders of magnitude less intense than the 46 800 cm^{-1} absorption, and this large difference in relative intensities permits us to assign the 30 190 cm^{-1} feature as the *d–d* transition ${}^2T_{2g}(\Gamma_8) \rightarrow {}^2E_g(\Gamma_8)$. The position of this absorption is very close to the shoulder reported by Moffitt. The two intense bands are similar to those observed by McDiarmid, and are assigned as $\pi(F) \rightarrow t_{2g}(Re)$ charge transfer.

The observation that the *d–d* band in ReF_6 is much weaker than the c.t. bands indicates that intense absorptions in other MF_6 species should be assigned as $\pi(F) \rightarrow$ M c.t. rather than *d–d* transitions. The t_{2g} orbitals in ReF_6 split under spin-orbit coupling into $\Gamma_8(-\frac{1}{2}\zeta)$ and $\Gamma_7(+\zeta)$ and, taking Moffitt's value of 5 000 cm^{-1} for the transition, ζ is estimated to be *ca.* 3 300 cm^{-1}. If one then ignores configurational interaction between the Γ_8 states in ${}^2T_{2g}$ and ${}^2E_g$, the ligand-field splitting $10Dq$ is estimated as *ca.* 28 000 cm^{-1}. This parameter[31] is expected to change only slowly through the sequence Re→Pt but the c.t. absorptions are expected to move significantly to lower energy. As a result, the *d–d* bands in the remaining hexafluorides are likely to be obscured by the more intense c.t. absorptions.

OsF_6. For the d^2 OsF_6 (μ = 1.50 B.M.) Moffitt *et al.*[15] identified three intra-configurational bands in the electronic spectrum. These originated from the ground state ${}^3T_{1g}\,(\Gamma_3)$, and these authors also observed higher energy absorptions at 35 700 and 40 800 cm^{-1}, which were assigned as *d–d* transitions ($t_{2g}{}^2 \rightarrow t_{2g}{}^1 e_g{}^1$). Subsequently, Eisenstein[33] confirmed the assignments of the low energy bands, but suggested that the absorptions above 35 000 cm^{-1} were due to charge transfer.

Our spectra of matrix-isolated OsF_6 differs significantly from that described by Moffitt *et al.*[15] In the high energy region we find bands at 36 230, 45 435, and *ca.* 51 000 but *no* band at 41 000 cm^{-1}. Extensive vibrational structure was observed on the 45 435 and 36 230 cm^{-1} bands with average spacings *ca.* 630 and 660 ($\pm$50) cm^{-1} respectively, and we assign all three high energy bands as $\pi(F) \rightarrow t_{2g}(Os)$ c.t. For OsF_6 in the ground state $\nu_1(Os\text{–}F, A_{1g})$ lies at 733 cm^{-1}.

Moffitt's feature at *ca.* 41 000 cm^{-1} arises, we believe, from OsO_4. As noted earlier, this species is a persistent impurity in osmium fluoride chemistry, and its u.v.–visible spectrum shows intense absorptions at 40 800 and 35 000 cm^{-1} which display characteristic vibrational structures.[26] No vibrational structure for any of the high energy bands was reported in the earlier work, but the most likely explanation for the discrepancy seems to be that the 'OsF_6' absorption at 40 800 cm^{-1} is the upper band of OsO_4, and the 35 700 cm^{-1} band is a composite of the second OsO_4 band at *ca.* 35 000 and the genuine OsF_6 band at *ca.* 36 200 cm^{-1}.

IrF_6. For IrF_6 (d^3) (μ = 2.9 B.M.) several structured absorptions lying below 20 000 cm^{-1} are assignable as intra-configurational bands arising from a ground state ${}^4A_{2g}(\Gamma_8)$.[15,19] Our nitrogen matrix spectra in this region (11 000—18 000 cm^{-1}) show several weak, sharp features which are in close agreement with those in the previous work, and need not be discussed further. The intense high energy bands at *ca.* 43 400 and *ca.* 35 700 cm^{-1} show vibrational progressions of *ca.* 650 cm^{-1} which correlate with the ground state A_{1g} mode in IrF_6 at 702 cm^{-1}, and are assigned as c.t. bands. Our spectra also show a distinct, relatively intense, shoulder at *ca.* 30 400 cm^{-1} which we similarly assign as $\pi(F) \rightarrow t_{2g}(Ir)$ c.t. rather than *d–d* (${}^4A_{2g} \rightarrow {}^4T_{2g}$) since a bathochromic shift in the lowest energy c.t. band is expected compared with OsF_6. This latter absorption has been assigned at *ca.* 36 200 cm^{-1}. These results are in close agreement with Moffitt's published spectra.[15]

PtF_6. Platinum hexafluoride is the least stable 5*d* hexafluoride, and has received less attention in the literature than the other members of the series. Its temperature independent magnetic moment of 1.4 B.M. indicates a ground state $^3T_{1g}(\Gamma_1)$ and Moffitt's gas phase spectrum[15] showed three intra-configurational bands in the region 3 000—6 000 cm^{-1} (Table 2) with spin-forbidden bands $^3T_{1g}(\Gamma_1) \longrightarrow {}^1T_{2g}, {}^1E_g$ at *ca.* 12 000 cm^{-1}. A third spin-forbidden band, $^3T_{1g}(\Gamma_1) \longrightarrow {}^1A_{1g}$ was just evident on the rising absorption above 16 000 cm^{-1}. In this lower energy region, our matrix spectra show features very similar to those found by Moffitt.

The higher energy region is unclear in Moffitt's spectrum. He reports a band at *ca.* 32 000 cm^{-1}, and an ill defined maximum at *ca.* 45 500 cm^{-1}, whilst a third band appears to lie in the region 17 000—25 000 cm^{-1} not covered in that study. At higher energy, we observe an intense band at 23 500 cm^{-1} with a shoulder at 26 250 cm^{-1}, a second intense band at *ca.* 32 900 cm^{-1}, and a rising absorption at >51 000 cm^{-1} which exhibits a shoulder at *ca.* 46 500 cm^{-1}. The 23 500, 26 250, and 32 900 cm^{-1} bands all show well resolved vibrational progressions of *ca.* 560 cm^{-1}. In the ground state, ν_1 (A_{1g}) lies at 656 cm^{-1}, and there is therefore a substantial bond weakening in the excited state in comparison with the other hexafluorides in this sequence.

The spectrum (Figure 3) also shows a long tail to low energy of the 23 500 cm^{-1} band, but this does not become more clearly resolved on extended deposition and is probably associated with the $^3T_{1g}(\Gamma_1) \longrightarrow {}^1A_{1g}$ transition rather than with a further c.t. band. The assignments of these higher energy bands are less obvious for PtF_6. The high intensities of 23 500 and 26 250 cm^{-1} bands clearly indicate $\pi(F) \longrightarrow t_{2g}(Pt)$ c.t. but the expected shifts to lower energy of *all* the charge-transfer bands mean that $\sigma(F) \longrightarrow t_{2g}(Pt)$ and $\pi(F) \longrightarrow e_g(Pt)$ transitions may now be sufficiently low in energy to fall within our spectral range.

There is no reliable estimate for $10Dq$ in PtF_6, but based on the value derived for ReF_6 (*ca.* 28 000 cm^{-1}, see above) it is possible that the rising absorption at >51 000 cm^{-1} may correspond to $\pi(F) \longrightarrow e_g(Pt)$. The shoulder at 46 500 cm^{-1} seems too *high* to be attributed to $\pi(F) \longrightarrow t_{2g}(Pt)$, and we provisionally assign it as $\sigma(F) \longrightarrow t_{2g}(Pt)$ as previously suggested by Allen and Warren.[27] The remaining high-energy feature at *ca.* 32 900 cm^{-1} shows a very similar vibrational progression to the 23 500 and 26 250 cm^{-1} bands, and we therefore assign it to a third $\pi(F) \longrightarrow t_{2g}(Pt)$ c.t. transition.

Finally, our spectra also showed a weak shoulder at *ca.* 27 700 cm^{-1} which is provisionally assigned as a *d–d* transition. In the isoelectronic ion IrF_6^-, there is[27] a $^3T_{1g} \longrightarrow {}^5E_g$ transition at 24 200 cm^{-1} which would be expected to represent a lower limit for the corresponding absorption in PtF_6.

$\chi_{opt.}$ *Values for* M^{6+}.—When spin pairing and relativistic effects are included,[34] the optical electronegativity formula predicts *lowest energy* F ⟶ M c.t. bands (ΔE in cm^{-1}), as follows:

$$ReF_6,\ \Delta E_{obs.} = 30\,000\,[\chi_{opt.}(F^-) - \chi_{opt.}(Re^{VI})] - \tfrac{2}{3}D - \tfrac{1}{2}\zeta$$

$$OsF_6,\ \Delta E_{obs.} = 30\,000\,[\chi_{opt.}(F^-) - \chi_{opt.}(Os^{VI})] - \tfrac{4}{3}D + \zeta$$

$$IrF_6,\ \Delta E_{obs.} = 30\,000\,[\chi_{opt.}(F^-) - \chi_{opt.}(Ir^{VI})] + 2D - 2\zeta$$

$$PtF_6,\ \Delta E_{obs.} = 30\,000\,[\chi_{opt.}(F^-) - \chi_{opt.}(Pt^{VI})] + \tfrac{2}{3}D + \zeta$$

The Racah parameter, D, and spin-orbit coupling parameter, ζ, are generally unavailable for the 5*d* hexafluorides, but if we adopt the value ζ *ca.* 3 300 cm^{-1} obtained here for ReF_6, and take D as *ca.* 2 500 cm^{-1} by extrapolation from the 3*d* and 4*d* fluoroanions,[27] our spectra may be used to refine the literature values of $\chi_{opt.}$ for Re, Os, Ir, and Pt.

Taking $\chi_{opt.}(F)$ to be 3.90, these are currently:[31] Re, 2.1; Os, 2.7; Ir, 2.95; and Pt, 3.3, and our refined values are calculated to be Re, 2.21; Os, 2.72; Ir, 2.80; and Pt, 3.31.

Although these numbers are based on estimated values of ζ and D, one can easily show that errors of up to ±10% in either of these parameters do not appreciably affect the $\chi_{opt.}$ values. This approach will therefore be of some value not only in spectral interpretation, but also in predicting the positions of c.t. bands in other M^{VI} complexes.

Acknowledgements

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