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# The Electronic Spectra of the Hexafluoroosmate(V) and Hexafluoroiridate(V) Anions

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The electronic spectra of the hexafluoroosmate(V) and hexafluoroiridate(V) anions have been studied by diffuse reflectance between 4 and 50 kK. For $OsF_6^-$ the relatively weak bands at 8.00, 10.3, 10.8, 16.3, and 18.2 kK are ascribed to formally spin-forbidden transitions within the $t_{2g}^3$ manifold, while a much stronger band at 37.5 kK, with a shoulder at 41.7 kK, is thought to involve both ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$, $t_{2g}^3 \rightarrow t_{2g}^2e_g$ excitations, as well as a Laporte-allowed charge-transfer transition. For $IrF_6^-$ the absorption at about 4 kK and the well-marked peak at 6.5 kK are assigned to transitions within the spin–orbit split ${}^3T_{1g}(t_{2g}^4)$ ground state, and the weaker bands at 12.9 and 19.8 kK to spin-forbidden transitions within the $t_{2g}^4$ subshell. The weak band at 24.1 kK is attributed to the ${}^3T_{1g}(t_{2g}^4) \rightarrow {}^5E_g(t_{2g}^3e_g)$ transition, and the fairly strong shoulder at about 33 kK to spin-allowed $t_{2g}^4 \rightarrow t_{2g}^3e_g$ excitations. It seems likely that the strong band with a maximum at 41.8 kK contains both charge-transfer and further $t_{2g}^4 \rightarrow t_{2g}^3e_g$ transitions. The bands were fitted using the complete strong-field electrostatic and spin–orbit matrices for $d^3$ and $d^4$ systems, assuming $C/B = 4.75$ and 4.90 for Os(V) and Ir(V), respectively, yielding for $OsF_6^-$ the parameters $Dq = 3500$ cm$^{-1}$, $B = 410$ cm$^{-1}$, and $\xi = 3200$ cm$^{-1}$ and for $IrF_6^-$ the values $Dq = 2850$ cm$^{-1}$, $B = 360$ cm$^{-1}$, and $\xi = 3400$ cm$^{-1}$. The degree of covalency indicated is high for fluoride complexes and comparable with that found for quadrivalent $MF_6^{2-}$ species of the 3d series.

## Introduction

For the hexahalo complexes of the 3d series the highest metal oxidation state encountered is IV, this being stabilized almost uniquely by the fluoride anion. In the 5d series, however, numerous metal(IV)–hexahalo species are known, and for the elements W to Pt the M(V) and M(VI) states are well established, although they are only represented by hexafluoro derivatives. These $MF_6$ entities thus once more permit the study of the high and less common oxidation states, with the expectation that the Laporte-allowed charge-transfer bands should lie at sufficiently high energies for some at least of the d–d transitions to be located, and a detailed study of the $MF_6$ compounds of Re, Os, Ir, and Pt has been carried out by Moffitt, *et al.*[2]

For the M(V), $MF_6^-$, series some spectroscopic results have been recorded by Brown, Russell, and Sharp,[3] but no diagramatic presentation of the spectra was made and in the analysis of the data spin–orbit coupling was treated as only a minor perturbation. Moreover, on reinvestigating the spectra of $OsF_6^-$ and $IrF_6^-$ over a wider energy range, we noted a number of significant differences between our results and those of Brown, *et al.*, and we therefore now report our findings for the hexafluoroosmate(V) and hexafluoroiridate(V) anions, together with the fitting parameters obtained using the complete strong-field electrostatic and spin–orbit matrices for $d^3$ and $d^4$ systems.

## Experimental Section

**Potassium and Cesium Hexafluoroosmate(V).**—These were obtained by the action of bromine trifluoride on 1:1 mixtures of KCl or CsCl and $OsBr_4$, according to the method of Hepworth, Robinson, and Westland.[4] *Anal.* Calcd for $KOsF_6$: Os, 55.4; F, 33.1. Found: Os, 55.3; F, 33.4. Calcd for $CsOSF_6$: Os, 43.5; F, 26.0. Found: Os, 43.8; F, 26.5.

**Cesium Hexafluoroiridate(V).**—This was prepared similarly[4] by the action of bromine trifluoride on a 1:1 mixture of CsCl and $IrBr_3$. *Anal.* Calcd for $CsIrF_6$: Ir, 43.9; F, 25.9. Found: Ir, 43.6; F, 26.2.

**Diffuse Reflectance Measurements.**—These were carried out as before[5,6] using a Beckman DK 2A spectroreflectometer with a magnesium oxide reference. Intensities are expressed in terms of the Kubelka–Munk function, $F_R$, but no attempt was made to convert these to approximate extinction coefficients because of the uncertainty concerning the scattering coefficient appropriate for 5d series compounds.

## Results and Discussion

For the $OsF_6^-$ ion the spectra of the potassium and cesium salts were virtually identical. We therefore list in Tables I and II the data for $CsOF_6$ and for $CsIrF_6$, the corresponding spectra being shown in Figures 1 and 2. In Figures 3 and 4 are shown the energy

TABLE I
THE DIFFUSE REFLECTANCE SPECTRUM
OF CESIUM HEXAFLUOROOSMATE(V)

| Band position, kK | $F_R$ | Assignment |
|---|---|---|
| 8.00 | 1.3 | ${}^4A_{2g}(\Gamma_8) \rightarrow {}^2T_{1g}(\Gamma_8)$ |
| 9.17 sh | 1.0 | |
| 10.30 | 1.65 | ${}^4A_{2g}(\Gamma_8) \rightarrow {}^2E_g(\Gamma_8)$ |
| 10.81 | 1.3 | ${}^4A_{2g}(\Gamma_8) \rightarrow {}^2T_{1g}(\Gamma_6)$ |
| 16.3 | 0.8 | ${}^4A_{2g}(\Gamma_8) \rightarrow {}^2T_{2g}(\Gamma_7)$ |
| 18.2 | 0.8 | ${}^4A_{2g}(\Gamma_8) \rightarrow {}^2T_{2g}(\Gamma_8)$ |
| 37.5 | 23.8 | ${}^4A_{2g}(\Gamma_8) \rightarrow {}^4T_{2g}$ |
| | | $\pi \rightarrow t_{2g}$ (?) |
| 41.7 sh | 21.0 | ${}^4A_{2g}(\Gamma_8) \rightarrow {}^4T_{1g}$ |

TABLE II
THE DIFFUSE REFLECTANCE SPECTRUM
OF CESIUM HEXAFLUOROIRIDATE(V)

| Band position, kK | $F_R$ | Assignment |
|---|---|---|
| 4.0 | 0.85 | ${}^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_4)$ |
| 6.25 sh, 6.55, 6.78 sh | 3.5 | ${}^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_5, \Gamma_3)$ |
| 7.40 sh | 2.0 | |
| 12.9 | 1.7 | ${}^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}(\Gamma_5)$, ${}^1E_g(\Gamma_3)$ |
| 19.8 | 3.0 | ${}^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}(\Gamma_1)$ |
| 24.2 | 3.2 | ${}^3T_{1g}(\Gamma_1) \rightarrow {}^5E_g(\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5)$ |
| 33.0 sh | 9.0 | ${}^3T_{1g}(\Gamma_1) \rightarrow$ lower $t_{2g}^3e_g$ triplet levels |
| 41.7 | 21.0 | ${}^3T_{1g}(\Gamma_1) \rightarrow$ higher $t_{2g}^3e_g$ triplet levels, $\pi \rightarrow t_{2g}$ (?) |

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[1] Ph.D. student supported by the Royal Saudi Arabian Government.

[2] W. Moffit, G. L. Goodman, M. Fred, and B. Weinstock, *Mol. Phys.*, **2**, 109 (1959).

[3] D. H. Brown, D. R. Russell, and D. W. A. Sharp, *J. Chem. Soc. A*, 18 (1966).

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[5] (a) G. C. Allen and K. D. Warren. *Inorg. Chem.*, **8**, 753 (1969); (b) G. C. Allen and K. D. Warren, *ibid.*, **8**, 1895 (1969).

[6] G. C. Allen and K. D. Warren, *ibid.*, **8**, 1902 (1969).

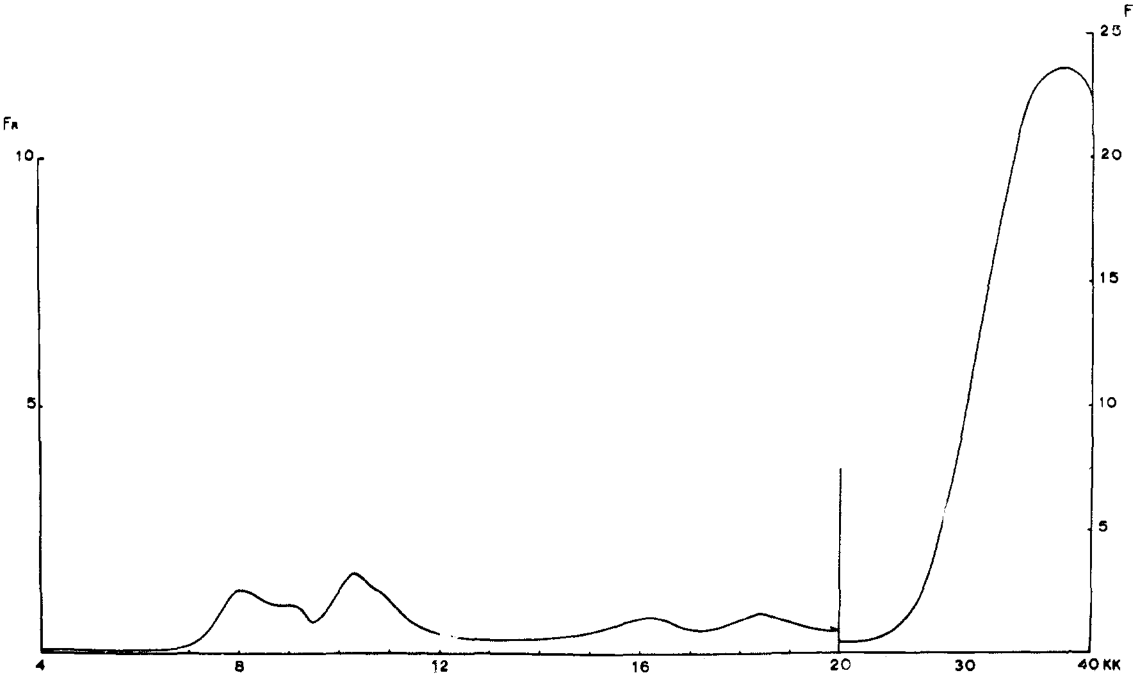

Figure 1.—The electronic spectrum of cesium hexafluoroosmate(V).

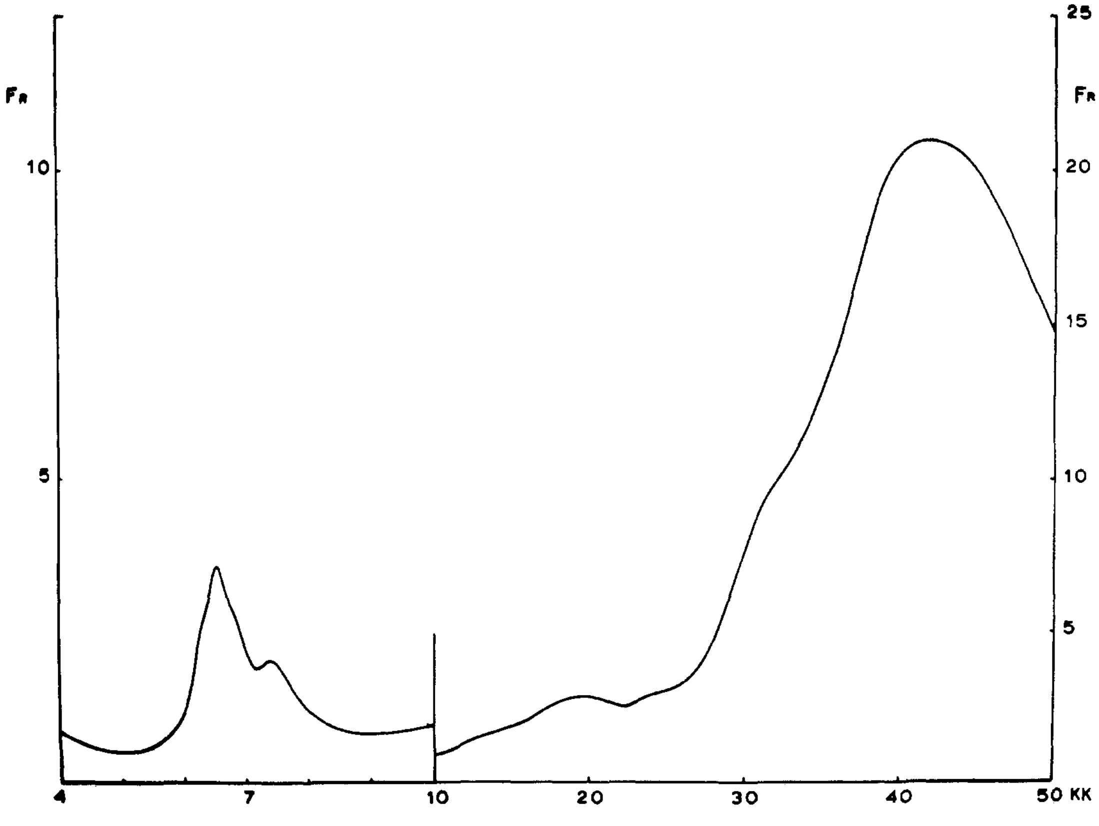

Figure 2.—The electronic spectrum of cesium hexafluoroiridate(V).

levels calculated for $OsF_6^-$ and for $IrF_6^-$, respectively, using the parameters indicated.

Comparison of these results with those of Brown, *et al.*,[3] reveals numerous discrepancies: their measurements were of course restricted to the region between 10 and 40 kK, but for $IrF_6^-$ they reported only two bands, at 21 and 30 kK, which they assigned as ${}^3T_{1g} \rightarrow {}^5E_g$ and ${}^3T_{1g} \rightarrow {}^3E_g$, ${}^3T_{2g}$, ${}^3A_{1g}$, and ${}^3A_{2g}$, while for $OsF_6^-$ bands at 10.4, 11.0, 18.0, 31.0, and 39.0 kK are assigned as transitions from ${}^4A_{2g}$ to ${}^2E_g$, ${}^2T_{1g}$, ${}^2T_{2g}$, ${}^4T_{1g}$, and ${}^4T_{1g}$ levels, respectively. For the corresponding region of our spectrum there is broad general agreement for $IrF_6^-$ since the most prominent features are the band at 19.8 kK and the shoulder at around 33 kK, but the other two bands, although somewhat obscured by a rather high background absorption, are clearly discern-

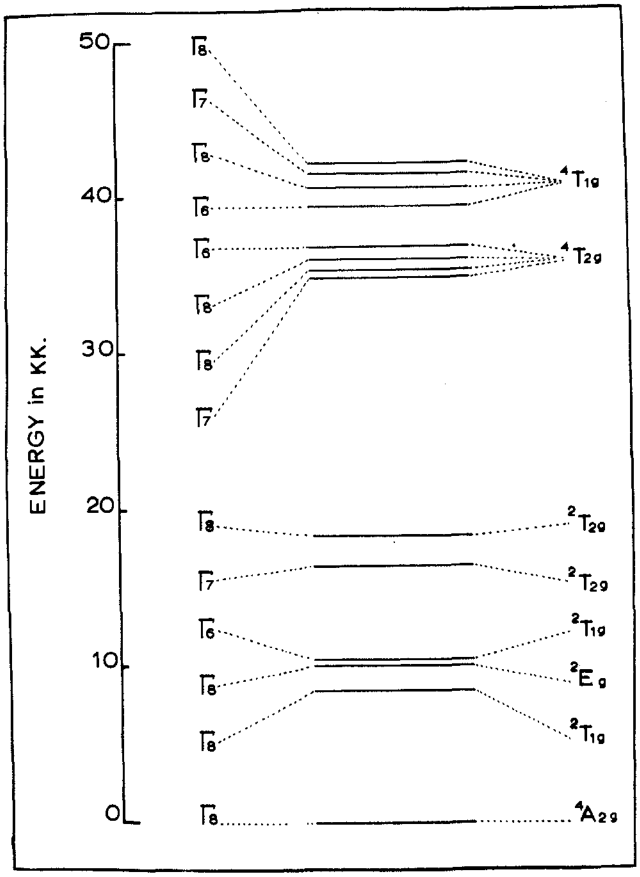

Figure 3.—Calculated energy levels for $OsF_6^-$; $Dq = 3500\ cm^{-1}$, $B = 410\ cm^{-1}$, $\xi = 3200\ cm^{-1}$, $C/B = 4.75$.

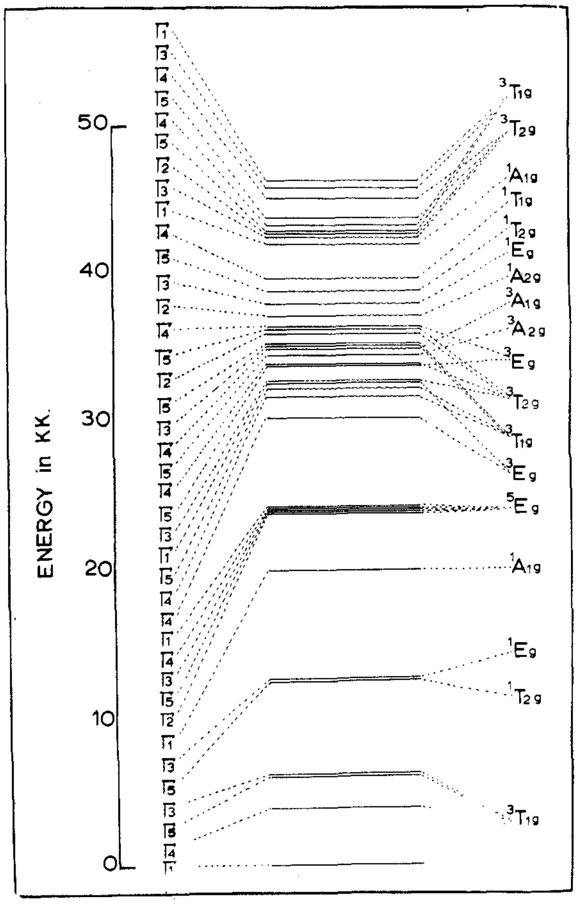

Figure 4.—Calculated energy levels for $IrF_6^-$; $Dq = 2850\ cm^{-1}$, $B = 360\ cm^{-1}$, $\xi = 3400\ cm^{-1}$, $C/B = 4.90$.

ible at 12.9 and 24.2 kK, while the extension of the coverage below 10 kK discloses a relatively strong absorption at about 7–8 kK and a further band near 4 kK. For $OsF_6^-$ our spectrum shows two well-defined bands at 16.3 and 18.2 kK, instead of the single absorption at 18.0 kK reported by Brown, *et al.*[3] Actually these are both quite sharp peaks, but this is to some extent concealed by the background absorption also found for $CsOsF_6$ and by the presentation to the spectrum in $F_R$ units on a rather expanded energy scale. In the higher energy region, although the band at 37.5 kK is very broad, we find no evidence of a distinct absorption near 31 kK, but below 10 kK an additional band system between 8 and 10 kK is revealed.

In the analysis of spectroscopic data for complexes of the 5d elements certain difficulties arise which are not encountered in the first transition series. In the first place the spin–orbit coupling constant, $\xi$, is now substantial, being comparable in magnitude to the crystal field splitting parameter, $Dq$, and appreciably greater than the Racah electrostatic parameter, $B$. Consequently spin–orbit coupling cannot be treated as a minor effect, and we therefore fitted our data using the $O_h$ strong field electrostatic repulsion matrices given by Tanabe and Sugano[7] and the $d^3$ and $d^4$ spin–orbit matrices of Eisenstein[8] and Schroeder,[9] respectively. In the 3d series the value of the ratio of the Racah repulsion parameters, $C/B$, is usually determined from the free-ion data listed by Tanabe and Sugano,[7] but for the 5d series no such data are available. For some treatments[10–12] of 5d complexes $B$ and $C$ have been allowed to vary independently, but this has led to wild variations in the $C/B$ ratio within series of closely related complexes and we therefore felt it safer to adopt the same value for $C/B$ as that appropriate for the corresponding $d^n$ ion of the 3d series. These values were obtained by extrapolation from the data of Tanabe and Sugano, this yielding $C/B = 4.75$ for Os(V) and 4.90 for Ir(V). In our fitting of the data we used throughout only a single value of $B$ and of $\xi$ for each complex. For both compounds all the bands below 20 kK relate to transitions within the $t_{2g}{}^n$ manifold (*vide infra*) for which $B_{55}$ and $\xi_{55}$ parameters are appropriate, and although it is likely that somewhat smaller values, $B_{35}$ and $\xi_{35}$, should relate to the higher energy $t_{2g}{}^n \rightarrow t_{2g}{}^{n-1}e_g$ transitions, we did not feel justified in making this refinement because of the impossibility of resolving the band structure in this region.

A further problem also occurs in assessing the extent of covalency effects. Normally the nephelauxetic ratio, $\beta$ $(=B_{\text{complex}}/B_{\text{gas}})$, and the corresponding relativistic ratio, $\beta^*$ $(=\xi_{\text{complex}}/\xi_{\text{gas}})$, may be used for this purpose, but values of the free-ion parameters are almost entirely lacking for the third transition series. We therefore

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adopted Jørgensen's[13] proposal, $B_{\text{gas}}(\text{M, 5d}^n) = 0.6B_{\text{gas}}(\text{M, 3d}^n)$, together with the Jørgensen–Racah[14] relationship for the calculation of $B_{\text{gas}}$ for the higher oxidation states of the 3d series, thus obtaining the results $B_{\text{gas}}(\text{Os(V)}) = 727\ \text{cm}^{-1}$ and $B_{\text{gas}}(\text{Ir(V)}) = 762\ \text{cm}^{-1}$. There are similarly hardly any values of the spin–orbit coupling constant for the free ions of the 5d elements, and we thus followed Dunn[15] in taking $\xi_{\text{gas}}(\text{Os(V)}) = 4500\ \text{cm}^{-1}$. From this, assuming the proportionality between $\xi$ and $B^3$ demonstrated by Cole and Garrett,[16] we obtain $\xi_{\text{gas}}(\text{Ir(V)}) = 5180\ \text{cm}^{-1}$, and these figures have been used for calculating $\beta$ and $\beta^*$.

The X-ray crystallographic data for a large number of $\text{MF}_6^-$ complexes of the 5d series have been summarized by Kemmitt, Russell, and Sharp,[17] and all the compounds studied here are known to have a rhombohedral, $\text{KOsF}_6$ type lattice, in which the $\text{MF}_6$ unit is slightly distorted from a regular octahedron by compression along the trigonal axis. Analysis of the data on the basis of $O_h$ symmetry about the metal should thus represent a satisfactory approximation, but the lower effective point symmetry may play some part in the splitting observed for the 8-kK band of $\text{OsF}_6^-$ and for the 6.5-kK band of $\text{IrF}_6^-$.

For the d$^3$ system, $\text{OsF}_6^-$, the relatively weak bands below 20 kK may readily be assigned as spin-forbidden transitions within the $\text{t}_{2\text{g}}{}^3$ subshell, since for the 5d series a $Dq$ value of about 3000 cm$^{-1}$ would be anticipated for fluoro complexes. These therefore correspond to transitions from the $^4\text{A}_{2\text{g}}$ ground state to the $^2\text{E}_\text{g}$, $^2\text{T}_{1\text{g}}$, and $^2\text{T}_{2\text{g}}$ levels, which in the octahedral double group, O*, give rise respectively to the states, $\Gamma_8$, $\Gamma_6 + \Gamma_8$, and $\Gamma_7 + \Gamma_8$. The best value of the spin–orbit coupling constant is determined primarily from the splitting of the $\Gamma_7$ and $\Gamma_8$ components of the $^2\text{T}_{2\text{g}}$ state, while the barycenter of this level affords a good estimate for $B$. For any reasonable choice of $B$ and $\xi$ the two $\Gamma_8$ levels arising from the $^2\text{E}_\text{g}$ and $^2\text{T}_{1\text{g}}$ states will lie some 1.5 kK apart, with the $\Gamma_6$ state only slightly above the upper $\Gamma_8$ level. Inspection of the eigenvectors from the diagonalization of the $\Gamma_8$ matrix showed the lower $\Gamma_8$ level to be predominantly $^2\text{T}_{1\text{g}}$ in character and the upper state primarily $^2\text{E}_\text{g}$. We therefore assign the peak at 10.3 kK as $^4\text{A}_{2\text{g}}(\Gamma_8) \rightarrow {}^2\text{E}_\text{g}(\Gamma_8)$ and the shoulder at 10.8 kK as $^4\text{A}_{2\text{g}}(\Gamma) \rightarrow {}^2\text{T}_{1\text{g}}(\Gamma_6)$, while the absorption between 8 and 9 kK corresponds to the $^2\text{T}_{1\text{g}}(\Gamma_8)$ level. The origin of the well-marked shoulder at 9.17 kK is harder to ascertain; the splitting seems unlikely to be due to the trigonal compression of the $\text{MF}_6$ unit since the spectra of the potassium and cesium salts are almost identical. It is possible that a Jahn–Teller splitting of the $\Gamma_8$ ground state is involved, but since this represents only a spin degeneracy, it would not be expected to be very large. Alternatively a dynamic effect may be involved, or the feature might represent imperfectly resolved vibrational substructure. Thus, for the isoelectronic $\text{ReF}_6{}^{2-}$ anion Jørgensen and Schwochau[18] observed considerable detail in the solution spectrum for the $^4\text{A}_{2\text{g}} \rightarrow {}^2\text{E}_\text{g}$, $^2\text{T}_{1\text{g}}$ band, which they attributed to vibrational structure, and it is noteworthy that the overall band shape is quite similar to that found here for $\text{OsF}_6^-$. However, lacking better resolution and information about the vibrational modes, it is not possible to make a more definite interpretation, and the most satisfactory fit of the observed bands was obtained using the parameters $Dq = 3500\ \text{cm}^{-1}$, $B = 410\ \text{cm}^{-1}$, and $\xi = 3200\ \text{cm}^{-1}$.

The value of $Dq$ assumed has of course little effect on the calculated positions of the intrasubshell ($\text{t}_{2\text{g}}{}^3$) transitions, but an appreciably smaller value, *ca.* 3100 cm$^{-1}$, would be required for the $^4\text{A}_{2\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$ band to be located at 31 kK. Since $Dq$ values of 3600 and 3280 cm$^{-1}$ are reported[2,18] for the isoelectronic $\text{IrF}_6$ and $\text{ReF}_6{}^{2-}$ systems, the intermediate figure of 3500 cm$^{-1}$ appears very reasonable, and $Dq$ for Os(V) would not be expected to be less than that for Re(IV). The shoulder at 41.7 kK could thus be assigned as $^4\text{A}_{2\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}$, and the calculated energy gap between the barycenters of the $^4\text{T}_{2\text{g}}$ and $^4\text{T}_{1\text{g}}$ levels is quite consistent with the observed band structure since a value of $B_{35}$ smaller than the $B_{55}$ parameter would tend to reduce this separation. However, the intensity of the absorption is abnormally high for a d–d transition, and it seems probable that a Laporte-allowed charge-transfer excitation is also involved, support for this view being provided by calculations based on optical electronegativities.

Thus, although $\chi_{\text{opt}}$ is not otherwise known for Os(V), the values of 2.2 and 2.6 recorded[19] for Os(IV) and Os(VI), respectively, permit an estimate to be made for the position of the lowest $\pi \rightarrow \text{t}_{2\text{g}}$ by interpolating $\chi_{\text{opt}}(\text{Os(V)})$ as 2.4. This however leads to a result of *ca.* 52 kK for $\pi \rightarrow \text{t}_{2\text{g}}$, taking $D$, the spin-pairing energy, to be 3.45 kK, as derived from out fitting parameters. Nevertheless, this figure and the $\chi_{\text{opt}}$ values for Os(IV) and Os(VI) given by Jørgensen[19] were obtained applying only the correction due to changes in the spin-pairing energy accompanying the $\text{d}^q \rightarrow \text{d}^{q+1}$ transition[20] and neglecting those due to relativistic (spin–orbit) terms. For $\text{t}_{2\text{g}}{}^n$ ground states these are readily obtained as outlined by Jørgensen[21] and by Jørgensen and Schwokau,[18] using the p$^n$ isomorphism and the approximation of jj coupling, in which the spin–orbit matrices are diagonal. In this way we find $\chi_{\text{opt}}(\text{Os(IV)}) = 2.29$ and $\chi_{\text{opt}}(\text{Os(VI)}) = 2.71$, so that taking $\chi_{\text{opt}}(\text{Os(V)}) \approx 2.5$ we obtain $\sigma_{\text{cor}} = 42$ kK. The spin-pairing correction of $-2D$ is now almost counterbalanced by the relativistic term of $+2\xi$, yielding the prediction $\sigma_{\text{obsd}} = 42.5$ kK, in excellent agreement with the position of the high-intensity absorption.

For the d$^4$ system, $\text{IrF}_6^-$, the magnetic data of Earnshaw, Figgis, Lewis, and Peacock[22] fully support the expected low-spin ground state, and the bands below 20 kK may thus be similarly classified as transitions within the $\text{t}_{2\text{g}}{}^4$ manifold, this giving rise to the states $^3\text{T}_{1\text{g}}$, $^1\text{T}_{2\text{g}}$, $^1\text{E}_\text{g}$, and $^1\text{A}_{1\text{g}}$. For the isoelectronic species $\text{OsCl}_6{}^{2-}$ Dorain and his coworkers[12] have shown that the $^1\text{A}_{1\text{g}}(\text{t}_{2\text{g}}{}^4)$ and $^5\text{E}_\text{g}(\text{t}_{2\text{g}}{}^3\text{e}_\text{g})$ levels are almost coincident, but an appreciably larger value of $Dq$ would be expected for $\text{IrF}_6^-$, thus supporting our assignment of the 24.2-

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(14) C. K. Jørgensen, *Helv. Chim. Acta, Fasciculus Extraordinarius A. Werner*, 131 (1967).

(15) T. M. Dunn, quoted by A. Earnshaw, *et al., J. Chem. Soc.*, 3132 (1961).

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(22) A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, *J. Chem. Soc.*, 3132 (1961).

kK band as $^3T_{1g} \rightarrow {}^5E_g$. Thus, since the $^1T_{2g}$ and $^1E_g$ levels would be expected to lie very close together, the rather weak bands at 12.9 and 19.8 kK are readily attributed to spin-forbidden $^3T_{1g} \rightarrow {}^1T_{2g}$, $^1E_g$, and $^3T_{1g} \rightarrow {}^1A_{1g}$ transitions. Thus, assuming that our band at 19.8 kK corresponds to the feature reported by Brown, *et al.*,[2] at 21 kK, we differ in its assignment. However, our calculations show that either a significantly smaller value of $Dq$ or an appreciably greater value of $B$—neither of which we consider realistic—would be required to maintain the $^3T_{1g} \rightarrow {}^5E_g$ assignment.

In the low-energy region, not studied by Brown, *et al.*, we find a fairly strong ($F_R \approx 3$) system of absorptions between 6 and 8 kK, which we attribute to transitions within the spin–orbit split $^3T_{1g}$ ground state, this assignment being supported by the intensity of the band which agrees with that anticipated for a formally spin-allowed transition. A similar result has been reported by Dickinson and Johnson[23] for $OsCl_6^{2-}$, as well as the examples noted by Moffitt, *et al.*,[2] and our own observations[24] have established the presence of similar low-energy bands for the $d^4$ and $d^5$ hexahalo complexes of Os(IV) and Ir(IV), and, as expected, their absence for the $d^6$ Ir(III) and Pt(IV) systems.

In both the $p^n(jj)$ and the strong-field scheme the total predicted splitting of the $^3T_{1g}$ ground state amounts to $^3/_2\xi$, $\Gamma_1$ lying lowest with the approximately degenerate $\Gamma_3$ and $\Gamma_5$ uppermost. This therefore provides a first-order estimate of the effective spin–orbit coupling constant, but in fact an intermediate coupling situation exists, and we thus used the complete strong-field matrices to fit the data. For the levels arising from $t_{2g}^4$ the predicted values are rather insensitive to the figure adopted for $Dq$, but the values used in Figure 4 were found to give a good fit of all low-energy bands and of the $^5E_g$ and the lower triplet, $t_{2g}^3e_g$, levels. The $\Gamma_4$ component of $^3T_{1g}$ is predicted at 4 kK and the start of a band in this region is evident. Unfortunately the extreme reactivity of $CsIrF_6$ frustrated our attempts to extend our measurements into the infrared region.

Once again the low-energy absorption displays a fairly complex structure, but with a $\Gamma_1$ ground state a static Jahn–Teller distortion cannot be responsible. There remain still the other possibilities considered for $OsF_6^-$, but in the absence of data concerning the vibrational modes further rationalization is not possible. For $IrF_6^-$ our fitting parameters predict $\Gamma_5$ and $\Gamma_3$ to lie slightly below the band maximum but, since these represent (0, 0) transitions, this is to be expected if, as usual, a (1, 0) $\tau_{1u}$ vibronically excited state makes the major contribution to the band intensity.

The fitting parameters used to reproduce the lower energy bands ($Dq = 2850\ \text{cm}^{-1}$, $B = 360\ \text{cm}^{-1}$, and $\xi = 3400\ \text{cm}^{-1}$) also predict a considerable number of triplet levels, arising from $t_{2g}^3e_g$, to lie between 30 and 36.5 kK, in good agreement with the prominent shoulder at about 33 kK. Above this we expect some rather weakly interacting singlet states between 37 and 42 kK, followed by further triplet levels from 42 to 47 kK. Thus both the position of the peak at 41.7 kK and its intensity tend to suggest its assignment as a $\pi \rightarrow t_{2g}$ excitation, although further d–d transitions are also probably present.

Again, no $\chi_{\text{opt}}$ value is available for Ir(V), but if we interpolate this as 2.63, using the values[19] $\chi_{\text{opt}}(\text{Ir(IV)}) = 2.35$ and $\chi_{\text{opt}}(\text{Ir(VI)}) = 2.90$, we predict $\pi \rightarrow t_{2g} = 42.5$ kK, using $D = 3.1$ kK as given by our data. In this case though the inclusion of the relativistic corrections affects the results in the opposite sense. Thus we find $\chi_{\text{opt}}(\text{Ir(IV)}) = 2.50$ and $\chi_{\text{opt}}(\text{Ir(VI)}) = 2.66$, and if we approximate $\chi_{\text{opt}}(\text{Ir(V)})$ as 2.58, we obtain $\sigma_{\text{cor}} = 39.6$ kK. This contains the spin-pairing correction, $-{}^4/_3D$, and the spin–orbit term, $-\xi$, thus giving a predicted $\sigma_{\text{obsd}}$ of 47.2 kK, which is again only slightly higher than the maximum of the high-intensity band.

From the free-ion values of $B$ and $\xi$ suggested above for Os(V) and Ir(V) it is possible to derive the nephelauxetic and relativistic ratios, $\beta$ and $\beta^*$, respectively, for the two complexes. These values will necessarily relate properly only to the $t_{2g}$ metal orbitals since they are derived primarily from the levels within the $t_{2g}^n$ manifolds, and for $OsF_6^-$ we thus obtain $\beta_{55} = 0.56$ and $\beta^*_{55} = 0.71$, and for $IrF_6^-$ $\beta_{55} = 0.47$ and $\beta^*_{55} = 0.66$. As expected both $\beta$ and $\beta^*$ decrease toward the end of the transition series, and the reduction from the free-ion value is much more marked for $\beta$ than for $\beta^*$. This latter follows since Jørgensen[13,19] has shown that if the effects of symmetry-restricted covalency are expressed *via* the Stevens delocalization coefficient, $a_5$, and that of central field covalency *via* the relative reduction in the effective nuclear charge ($Z^*_{\text{complex}}/Z^*_{\text{gas}}$), then $\beta \approx a_5^4(Z^*_{\text{complex}}/Z^*_{\text{gas}})$ and $\beta^* \approx a_5^2(Z^*_{\text{complex}}/Z^*_{\text{gas}})^2$, and $a_5$ should be appreciably less than unity for M(V) complexes.

By combining the above relations we obtain for $OsF_6^-$ the results $a^2 = 0.765$ and $Z/Z_0 = 0.965$, and for $IrF_6^-$ $a^2 = 0.70$ and $Z/Z_0 = 0.97$. The central field effect thus appears to be remarkably small, although this is not unreasonable for the more diffuse 5d orbitals, while the extent of symmetry-restricted covalency slightly exceeds that deduced[4,6] for the metal(IV)–fluoro complexes of the 3d series. It may be noted that the approximate expression for $\beta^*$ ignores any contribution by the ligands to $\xi$, but for fluoride ions the spin–orbit coupling constant is negligible in comparison to that of the metal.

It is nevertheless arguable whether one is justified in combining the expressions for $\beta$ and $\beta^*$ since the parameters of electrostatic repulsion are proportional to $\langle r^{-1}\rangle$ and the spin–orbit coupling constant is proportional to $\langle r^{-3}\rangle$. The former will therefore be predominantly an outer and the latter primarily an inner radial function, and it is questionable whether the same value of $Z/Z_0$ will be appropriate in both cases. One would on these grounds expect $Z/Z_0$ to differ little from unity in the $\beta^*$ relation, but it is unfortunately difficult to make any independent estimate of $a_5^2$. Thus, in the magnetic work of Figgis, Lewis, and Mabbs[25] on $OsF_6^-$ and of Earnshaw, Figgis, Lewis, and Peacock[22] on $IrF_6^-$, the extent of delocalization of the $t_{2g}$ metal orbitals onto the ligands is expressed in terms of the orbital reduction factor, $k$, which is assumed to be equivalent to $a_5^2$. With the simplyfing but unsubstantiated assumption that both $B$ and $\xi$ are reduced from the free-ion values by the factor $k$, it was found *via* an intermediate coupling scheme that the magnetic moment of $IrF_6^-$ could be closely reproduced using the free-ion values of the

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parameters, while for $OsF_6^-$ the data required $a_3^2k$ = 0.4. However, the latter result proved very sensitive to the values assumed for the free-ion parameters and was felt to be too low, while the estimation of $a_5^2$ is not possible in any case. Moreover, Gerloch and Miller[26] have shown that the presumed equivalence of $k$ and $a_5^2$ is invalid and that the extent of delocalization of the $t_{2g}$ set is normally appreciably underestimated by the orbital reduction factor.

Consequently the effective spin-orbit coupling constants for $OsF_6^-$ and $IrF_6^-$ can probably be determined more accurately from the electronic spectra, especially for $IrF_6^-$ where the spin-orbit splitting of the ground state is directly observable. Naturally the extent of the estimated nephelauxetic and relativistic effects depends closely on the free-ion parameters assumed, which are subject to an appreciable uncertainty. We are therefore attempting to assess the consistency of our parameterization by studying other 5d hexahalo complexes,[24] particularly those of Os(IV) and Ir(IV) in which the spin-orbit splitting of the ground levels allows good estimates of the effective spin-orbit coupling constants of the complexes to be made.

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# Vapor-Phase Raman Spectra, Force Constants, and Values for Thermodynamic Functions of the Tetrachlorides, Tetrabromides, and Tetraiodides of Titanium, Zirconium, and Hafnium

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The Raman spectra of titanium tetrachloride (at 65°), titanium tetrabromide (at 125°), and the tetrachlorides, tetrabromides, and tetraiodides of zirconium and hafnium (at 380–420°) have been recorded in the vapor phase, and values for all the fundamentals of these molecules are presented. The $\nu_2$(e) and $\nu_4(t_2)$ modes have pronounced rotational structure in each case. Although the zirconium and hafnium tetrahalides are polymeric in the solid state, their Raman spectra are interpreted to indicate that all are tetrahedral monomers in the vapor phase and thus isostructural with the titanium tetrahalides (which are tetrahedral in all states of matter). Force constants have been calculated for all the halides, including titanium tetraiodide (by the use of solution data) on the bases of both the modified-valence force field as well as the Urey–Bradley force field. Values for various thermodynamic functions have also been computed for each halide.

The tetrahalides of zirconium and hafnium have closely similar physical properties on account of the near identity of the radii of the two group IV metal atoms. In view of the technological interest in the separation of zirconium from hafnium and the role of the tetraiodides in the van Arkel–de Boer process for the preparation of the pure metals, the thermodynamic properties of the tetrahalides in the vapor phase acquire considerable practical importance. The properties may be calculated from a knowledge of the frequencies of the various fundamentals for molecules of known structure. Although the tetrahalides of titanium are tetrahedral monomers in all states of matter,[1] this is not the case for those of zirconium and hafnium. In the solid state, the halides $MX_4$ (M = Zr or Hf, X = Cl or Br) consist[2] of zigzag chains, each metal atom being octahedrally coordinated to halogen atoms, two of which are terminal and two bridging, *viz.* $[MX_{4/2}X_2]_\infty$. The structures of the solid tetraiodides are uncertain. By contrast with the data for the solid state, electron diffraction data on zirconium tetrachloride[3-5] and on hafnium tetrachloride[5] indicate that in the vapor phase these molecules are monomeric and tetrahedral. Infrared data[6] on the same two halides in the vapor phase have been interpreted on this basis, one fundamental, $\nu_3(t_2)$, having been found directly in each case. Vapor density measurements on zirconium tetrabromide and zirconium tetraiodide have shown that these halides also are monomeric in the vapor phase.[7] It remains to be shown that they, as well as the tetrabromides and tetraiodides of hafnium, are tetrahedral in the vapor phase. The present Raman data establish this conclusively.

Values for all the fundamentals of the group IVa tetrahalides (excepting the fluorides) have been determined, and appropriate force constants have been calculated on the modified-valence force field and Urey–Bradley force-field models. Values for various thermodynamic functions of each of the halides have also been calculated and are tabulated. A preliminary publication on this work has appeared.[8]

## Experimental Section

**Compounds.**—The sources of the tetrahalides were as follows: British Drug Houses ($TiCl_4$, $ZrCl_4$); Alfa Inorganics ($TiBr_4$, $TiI_4$, $ZrBr_4$, $ZrI_4$, $HfCl_4$, $HfBr_4$, and $HfI_4$).

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