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Electronic Spectra of Some Hexafluoro Anions of the 4d Series

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The electronic spectra of the hexafluoro anions of ruthenium(III), -(IV), and -(V) and of rhodium(IV) have been studied by diffuse reflectance between 4 and 50 kK. For RuF_6^{3-} weak bands near 10 kK and at 15.4 kK are identified as spin-forbidden $^2T_{2g} \rightarrow {}^4T_{1g}$ and $^2T_{2g} \rightarrow {}^4T_{2g}$ transitions, and stronger bands at 20.0, 26.5, and 34.0 kK are assigned as arising from groups of spin-allowed $t_{2g}{}^5 \rightarrow t_{2g}{}^4e_g$ excitations, namely, $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$, $^2T_{2g}$; $^2T_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$, $^2T_{2g}$; and $^2T_{2g} \rightarrow {}^2A_{1g}$, ^2E_g, respectively. For RuF_6^{2-} the weak broad band at 9.8 kK corresponds to the spin-forbidden transitions, $^3T_{1g} \rightarrow {}^1E_g$, $^1T_{2g}$, ^5E_g, and the stronger absorptions at 26.8, 31.0, and 38.8 kK to spin-allowed $t_{2g}{}^4 \rightarrow t_{2g}{}^3e_g$ transitions, $^3T_{1g} \rightarrow {}^3E_g$, $^3T_{1g}$, $^3T_{2g}$; $^3T_{1g} \rightarrow {}^3A_{1g}$, $^3A_{2g}$, ^3E_g; and $^3T_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$. For RuF_6^- low intensity spin-forbidden absorptions, $^4A_{2g} \rightarrow {}^2E_g$, $^4A_{2g} \rightarrow {}^2T_{1g}$, and $^4A_{2g} \rightarrow {}^2T_{2g}$, are identified at 9.2, 10.1, and 15.7 kK, respectively, while the stronger bands at 26.4 and 32.0 kK are assigned as the spin-allowed, $t_{2g}{}^3 \rightarrow t_{2g}{}^2e_g$, transitions, $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$. For RhF_6^{2-} the spin-forbidden $^2T_{2g} \rightarrow {}^4T_{1g}$ and $^2T_{2g} \rightarrow {}^4T_{2g}$ transitions appear as weak bands at 11.6 and 16.0 kK, and the stronger absorptions at 19.2, 21.2, 27.6, and 32.8 kK are assigned to the transitions $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$; $^2T_{2g} \rightarrow {}^2T_{2g}$, ^2E_g; $^2T_{2g} \rightarrow {}^2T_{1g}$, $^2T_{2g}$, $^2A_{1g}$; and $^2T_{2g} \rightarrow {}^2E_g$, respectively. Both RuF_6^{2-} and RhF_6^{2-} show indications of moderately strong bands below 4kK which in each case are assigned as transitions between the spin–orbit components of the ground states. The d–d bands were fitted using the strong field O_h matrices of Tanabe and Sugano, assuming $C/B = 4.75$ for the ruthenium complexes and 4.90 for the rhodium compound. The parameters thus obtained were: RuF_6^{3-} $Dq = 2200\ cm^{-1}$, $B = 550\ cm^{-1}$, $\beta = 0.80$; RuF_6^{2-} $Dq = 2500\ cm^{-1}$, $B = 500\ cm^{-1}$, $\beta = 0.68$; RuF_6^- $Dq = 2600\ cm^{-1}$, $B = 425\ cm^{-1}$, $\beta = 0.55$; and RhF_6^{2-} $Dq = 2050\ cm^{-1}$, $B = 410\ cm^{-1}$, $\beta = 0.54$. Intense absorptions, identified as Laporte-allowed, $\pi \rightarrow t_{2g}$, charge-transfer transitions, were found as follows: RuF_6^{3-}, >50 kK; RuF_6^{2-}, 48.0 kK; RuF_6^-, 40.0, *ca.* 50 kK; and RhF_6^{2-}, 39.6, 44.6 kK. The degree of covalency indicated by the results is discussed in conjunction with other data for 4d hexafluoro species, and the relationship between nephelauxetic ratios and optical electronegativities is further examined.

Introduction

The electronic spectra of the hexafluoro anions of the 3d series, showing the oxidation states III and IV, have already been extensively investigated,[2–6] and we have recently reported the results of similar studies of hexafluoro species in the 5d series for the oxidation states IV and V of Os and Ir.[7,8] In the 4d series the oxidation states exhibited by hexafluoro compounds range from III to the difficultly accessible VI, but, although spectra have been recorded for Mo(III),[9] Rh(III),[10] Ag(III),[4] Tc(IV),[11] and Tc(V),[12] the only comprehensive study so far carried out is that due to Brown, Russell, and Sharp.[13] These authors examined the hexafluoro complexes of Mo(V), Ru(V), Ru(IV), Rh(IV), and Pd(IV), together with a number of 5d compounds, but in no cases were the spectra presented diagrammatically, and the measurements covered only the restricted range of 10–40 kK.

It therefore became our objective to reexamine the d–d spectra of a number of 4d hexafluoro anions, over a wider energy range, in order to establish definitive values of the ligand field parameters, *Dq* and *B*, and thus of the nephelauxetic ratio, β. Moreover, it was also desirable to determine where possible the positions of the Laporte-allowed charge-transfer bands in order to ascertain whether the interpretation advanced[5,14] for 3d complexes remained valid in the second transition series and to test further the relationship between β and optical electronegativity, χ, there[5,14] established. Consequently, we have measured the electronic spectra of the potassium salts of the Ru(V) and Ru(IV) anions, RuF_6^- and RuF_6^{2-}, and of the cesium salt of the Rh(IV) anion, RhF_6^{2-}, which differ in a number of features from those of Brown, *et al.*,[13] and these are now reported together with the hitherto unrecorded spectrum of the Ru(III) complex, RuF_6^{3-}.

Experimental Section

Hexafluorometalate Salts. These were prepared according to literature procedures, and all gave satisfactory analytical figures for both fluorine and the transition metal. Potassium hexafluororuthenate(V) was obtained as a cream-colored solid by the action of bromine trifluoride on a 1:1 mixture of ruthenium and KCl, according to the method of Hepworth, Peacock, and Robinson,[15] and its hydrolysis following the same authors afforded the pale yellow potassium hexafluororuthenate(IV). Potassium hexafluororuthenate(III) was obtained as a dark solid by fusion of ruthenium trichloride with KHF_2 in a stream of nitrogen, following the method outlined by Peacock,[16,17] and cesium hexafluororhodate(IV) as a pale yellow solid by the action of bromine trifluoride on a 2:1 mixture of CsCl and rhodium trichloride as described by Sharpe,[18] and by Peacock.[17]

Diffuse Reflectance Measurements. These were carried out as before[2–8] using a Beckman DK 2A spectroreflectometer with a magnesium oxide reference. Intensities are expressed in terms of the Kubelka-Munk function, F_R, but, as for the 5d series,[7,8] uncertainty concerning the appropriate value of the scattering coefficient prevents their conversion to approximate extinction coefficients.

Results and Discussion

In Figure 1 and in Tables I–IV are presented the diffuse reflectance spectra of $KRuF_6$, K_2RuF_6, K_3RuF_6, and

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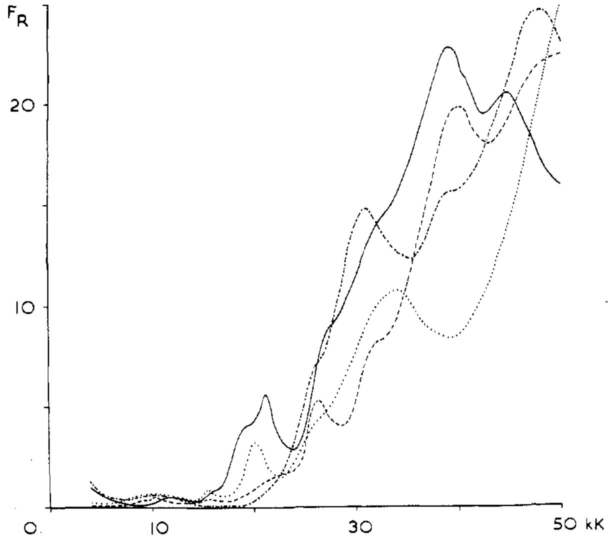

Figure 1. The electronic spectra of $KRuF_6$ (– – –), K_2RuF_6 (· – · –), K_3RuF_6 (· · · · ·), and Cs_2RhF_6 (——).

Table I. Diffuse Reflectance Spectrum of Potassium Hexafluororuthenate(V)

Band position, kK			
Obsd	Calcd^a	F_R	Assignment
9.2	9.4 (Γ_8)	0.3	$^4A_{2g} \rightarrow {}^2E_g$
10.1	9.6 (Γ_8) 9.9 (Γ_6)	0.5	$^4A_{2g} \rightarrow {}^2T_{1g}$
15.7	15.4 (Γ_8) 15.5 (Γ_7)	0.4	$^4A_{2g} \rightarrow {}^2T_{2g}$
(22.0)		1.5	?
26.4	26.1	5.3	$^4A_{2g} \rightarrow {}^4T_{2g}$
32.0 (sh)	31.0	8.2	$^4A_{2g} \rightarrow {}^4T_{1g}$
40.0		19.8	$\pi \rightarrow t_{2g}$
~50		22.5	$\pi \rightarrow t_{2g}$ or $\sigma \rightarrow t_{2g}$

^{a} $Dq = 2600$ cm^{-1}, $B = 425$ cm^{-1}, $\xi = 1000$ cm^{-1}, $C/B = 4.75$.

Table II. Diffuse Reflectance Spectrum of Potassium Hexafluororuthenate(IV)

Band position, kK			
Obsd	Calcd^a	F_R	Assignment
<4.0	1.7 (Γ_3,Γ_5)		$^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$
9.8 (br)	8.2 8.8 (Γ_3) 12.0–12.1 (Γ_2, Γ_5, Γ_3, Γ_4, Γ_1)	0.6	$^3T_{1g} \rightarrow {}^1T_{2g}$ $^3T_{1g} \rightarrow {}^1E_g$ $^3T_{1g} \rightarrow {}^5E_g$
26.8 (sh)	24.0, 24.7, 25.3	7.5	$^3T_{1g} \rightarrow {}^3E_g, {}^3T_{1g}, {}^3T_{2g}$
31.0	26.0, 27.0, 28.2	14.8	$^3T_{1g} \rightarrow {}^3A_{1g}, {}^3A_{2g}, {}^3E_g$ (?)
38.8	35.3, 35.6	15.6	$^3T_{1g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$ (?)
48.0		24.8	$\pi \rightarrow t_{2g}$

^{a} $Dq = 2500$ cm^{-1}, $B = 500$ cm^{-1}, $\xi = 1000$ cm^{-1}, $C/B = 4.75$.

Cs_2RhF_6, together with the corresponding band assignments. Also listed in Tables I-IV are the calculated band positions obtained in fitting the experimental data using the Tanabe-Sugano[19] strong field O_h matrices, including the spin-orbit interactions as given by Schroeder[20] and by Eisenstein.[21] For the lower energy levels we list the calculated positions for the individual double group components, but otherwise the figures given relate to the calculated barycenters of the levels.

Table III. Diffuse Reflectance Spectrum of Potassium Hexafluororuthenate(III)

Band position, kK			
Obsd	Calcd^a	F_R	Assignment
10.0	10.3 (Γ_8) 10.5 (Γ_6) 11.5 (Γ_8) 11.7 (Γ_7)	0.6	$^2T_{2g} \rightarrow {}^4T_{1g}$
15.4	15.3 (Γ_7) 15.4 (Γ_8) 15.6 (Γ_8) 15.6 (Γ_6)	0.9	$^2T_{2g} \rightarrow {}^4T_{2g}$
20.0	20.4, 20.4, 22.1	3.2	$^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}, {}^2T_{2g}$
26.5 (sh)	23.4, 27.0, 28.8	4.4	$^2T_{2g} \rightarrow {}^2E_g, {}^2T_{1g}, {}^2T_{2g}$
34.0 (br)	30.4, 35.2	10.8	$^2T_{2g} \rightarrow {}^2A_{1g}, {}^2E_g$ (?)
>50.0		25	$\pi \rightarrow t_{2g}$

^{a} $Dq = 2200$ cm^{-1}, $B = 550$ cm^{-1}, $\xi = 1000$ cm^{-1}, $C/B = 4.75$.

Table IV. Diffuse Reflectance Spectrum of Cesium Hexafluororhodate(IV)

Band position, kK			
Obsd	Calcd^a	F_R	Assignment
<4.0	1.8 (Γ_8)		$^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$
11.6	11.9 (Γ_8) 12.2 (Γ_7) 12.6 (Γ_8) 12.9 (Γ_6)	0.5	$^2T_{2g} \rightarrow {}^4T_{1g}$
16.0	15.5 (Γ_6) 15.5 (Γ_8) 15.8 (Γ_8) 15.9 (Γ_7)	0.8	$^2T_{2g} \rightarrow {}^4T_{2g}$
19.2	19.4, 19.5	4.0	$^2T_{2g} \rightarrow {}^2T_{1g}, {}^2A_{2g}$
21.2	20.8, 21.8	5.6	$^2T_{2g} \rightarrow {}^2T_{2g}, {}^2E_g$
27.6 (sh)	24.5, 25.9, 27.2	9.0	$^2T_{2g} \rightarrow {}^2T_{1g}, {}^2T_{2g}, {}^2A_{1g}$
32.8 (sh)	31.6	14.8	$^2T_{2g} \rightarrow {}^2E_g$ (?)
39.6		22.8	$\pi \rightarrow t_{2g}$
44.6		20.6	$\pi \rightarrow t_{2g}$

^{a} $Dq = 2050$ cm^{-1}, $B = 410$ cm^{-1}, $\xi = 1000$ cm^{-1}, $C/B = 4.90$.

For the compounds studied here spin-orbit effects are unlikely to be large enough to produce observable band splittings, even when the absorptions do not, as commonly happens, overlap, since the free ion values of ξ are probably some three to four times smaller than for the previously studied[7,8] 5d complexes. Thus, for Ru(III), Ru(IV), and Rh(IV), respectively, Dunn[22] estimates the free ion ξ values as 1180, 1350, and 1570 cm^{-1}, and the most obvious effect of the fairly large ξ lies in a moderate enhancement of the intensities of the spin-forbidden bands, as compared with many of those in the first transition series. For all the complexes studied here the value of ξ will, of course, be reduced to some extent due to covalency, the more so for the higher oxidation states. Therefore, lacking any more reliable estimate we have adopted the value $\xi = 1000$ cm^{-1} throughout our calculations.

In our calculations the value of the ratio of the Racah electrostatic repulsion parameters, C/B, has in each case been derived on the same basis as before,[7] that is, by adopting the same value as for the corresponding d^n ion of the 3d series, these in turn being obtained where necessary by extrapolation from the data of Tanabe and Sugano.[19] The values used were $C/B = 4.75$ for all the ruthenium complexes and 4.90 for $RhF_6{}^{2-}$; in some cases it would have been possible to produce significantly better fits to the experimental band positions by allowing B and C to vary independently, but as explained before[7] we were reluctant to do this because of the likelihood of encountering wildly

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varying values of *C*/*B* within a series of closely related compounds.

All the calculations were carried out on the basis of a regular O_h geometry for the MF_6 anion unit; $KRuF_6$ possesses a $KOsF_6$ type lattice with a 7° rhombohedral distortion of the anion unit, but with all the Ru–F distances equal,[23] while Cs_2RhF_6 shows a trigonal K_2GeF_6 type lattice,[24] and K_2RuF_6 displays either this same lattice or a cubic K_2SiF_6 structure.[25] For K_3RuF_6 there is some uncertainty concerning the lattice structure, but it certainly belongs to one of the cryolite type forms.[26]

We have also discounted the operation of any appreciable Jahn–Teller effects, certainly as far as the ground states are concerned, and there is no evidence to suggest that excited state effects are likely. Thus, for the d^4 and d^5 systems the ground states are respectively $^3T_{1g}$ and $^2T_{2g}$, which involve t_{2g} orbital degeneracies, and generally lead only to quite small Jahn–Teller splittings, while for the d^3 case the ground state $^4A_{2g}$ is an orbital singlet. Furthermore, the inclusion of spin-orbit coupling reinforces these conclusions; for d^4 and d^5 systems the ground states are split by spin-orbit coupling and in the O^* double group the lowest lying components are respectively the Jahn–Teller impotent Γ_1 and Γ_7 levels. For d^3 systems the $^4A_{2g}$ ground state transforms as Γ_8 in O^*, which could in principle be Jahn–Teller active, but is not expected to show appreciable splitting since it arises from an A_{2g} state.

Consideration of our experimental results in comparison with those of Brown, *et al.*,[13] discloses a number of significant differences: in the 10–40-kK region their listed band positions broadly correspond to our spectra, but in each case the latter show either new bands or additional resolution of the reported absorptions. In the region below 10 kK extra spin-forbidden bands are identified for RuF_6^- and RuF_6^{2-}, and for RuF_6^{2-} (d^4) and RhF_6^{2-} (d^5) the absorption at 4 kK indicates the beginning of a lower energy peak which we ascribe to transitions between the spin-orbit split components of the ground state. Similarly, above 40 kK, we have located Laporte-allowed charge-transfer bands for the three compounds studied by Brown *et al.*,[13] and for RuF_6^{3-} the start of an intense higher energy band is evident at 50 kK. In this context it should be noted that the intensities of the higher energy bands will appear to be underestimated on the F_R scale, relative to the lower d-d bands; this, as explained earlier,[5] is due to the progressive increase in the scattering coefficient which tends to occur above about 30 kK.

For the d^3 hexafluororuthenate(V) anion, RuF_6^-, Brown, *et al.*, reported bands at 10.4 and 15.4 kK which they attributed to spin-forbidden excitations.[13] These correspond closely to our peaks at 10.1 and 15.7 kK, but below 10 kK an additional distinct absorption is located at 9.2 kK, all three bands being of relatively low intensity. These peaks, at 9.2, 10.1, and 15.7 kK, are therefore assigned as spin-forbidden transitions within the t_{2g}^3 subshell, namely, $^4A_{2g} \rightarrow {}^2E_g$, $^4A_{2g} \rightarrow {}^2T_{1g}$, and $^4A_{2g} \rightarrow {}^2T_{2g}$. The two higher bands were reported by Brown, *et al.*,[13] to be of relatively high intensity, but our spectrum, presented as is proper on the F_R scale, does not bear this out; the bands are certainly somewhat stronger than is usually found for the 3d series,[2–5] but relative to the spin-allowed d-d bands they are only slightly more intense, as would indeed be expected due to the rather larger spin-orbit coupling constant. In fact, the eigenvectors obtained by diagonalization of the complete energy matrices show that the components of the three spin-forbidden bands contain on the average some 0.5% of quartet character; bearing in mind that these transitions are intrasubshell excitations, with band widths about an order of magnitude less than the $t_{2g}^3 \rightarrow t_{2g}^2e_g$ transitions, the observed intensities are clearly quite reasonable.

For the broad absorption at 22.0 kK there is no explanation from traditional ligand field theory. Brown, *et al.*,[13] explained a similar mysterious band in this region as being due to the lattice distortion of the RuF_6^- unit,[23] this causing a splitting of the $^4T_{2g}$ level. We are though doubtful whether this would be sufficient to produce an effect of this magnitude and incline to ascribe the absorption to traces of impurity. Similarly, for the reasons outlined above we feel it improbable that Jahn–Teller effects are responsible. However, a reviewer (whom we thank) has suggested the possibility of single-photon two-ion electronic excitations, which should occur at energies roughly twice that of the single-ion quartet doublet transitions.

The peak at 26.4 kK and the shoulder at 32.0 kK compare with values of 25.2 and 33.3 kK found by Brown, *et al.*, and are clearly the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, $t_{2g}^3 \rightarrow t_{2g}^2e_g$, transitions. The shoulder at 32.0 kK is somewhat higher in energy than the calculated value, but the proximity of the band to the intense absorption at 40.0 kK will cause it to appear to be drawn to higher energies. Since no further spin-allowed one-electron excitations are predicted for d^3 systems above the $^4A_{2g} \rightarrow {}^4T_{1g}$ transition, the intense band at 40.0 kK can confidently be assigned as a Laporte-allowed $\pi \rightarrow t_{2g}$ charge-transfer transition. The peak just above 50 kK, whose beginning is apparent in Figure 1, is most probably also of this type since it does not lie far enough above the 40-kK peak to represent a $\pi \rightarrow e_g$ band, although a $\sigma \rightarrow t_{2g}$ assignment would be possible.

For the d^4 hexafluororuthenate(IV) anion, RuF_6^{2-}, the magnetic moment[27] of 2.86 BM clearly indicates a low-spin, t_{2g}^4, $^3T_{1g}$ ground state. Under the influence of spin-orbit coupling this will be split into the double group components Γ_1, Γ_4, Γ_3, and Γ_5, of which the latter two are degenerate in the first order and Γ_1 lies lowest. The overall splitting of the ground state amounts to $(^3/_2)\,\xi$, to the first order, and assuming $\xi = 1000\ \text{cm}^{-1}$, the $^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3,\Gamma_5)$ transition would be expected at about 1.5 kK. However, second-order perturbation theory and our previous experience[7,8] with IrF_6^- and OsF_6^{2-} suggest that this is something of an underestimate, and diagonalization of the full energy matrices gives the value of 1.7 kK. Thus if, as is often found for d-d bands, the transition is τ_{1u} vibronically enabled and the (1,0) excited state makes the major contribution to the band intensity, the band will lie some 500 cm^{-1} above the calculated energy in any case, probably in the region of 2.0–2.5 kK. In fact, the start of a band at lower energy is clearly discernible near 4 kK in the spectrum of K_2RuF_6, and since the $^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3,\Gamma_5)$ excitation is known[7,8] to lead to quite broad absorptions for OsF_6^{2-} and IrF_6^-, there is good evidence to support this assignment in the present case. Note that no similar splitting would be expected for d^3 ions since the $^4A_{2g}$ ground state becomes Γ_8 in O^* and is not split.

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At higher energies our spectrum shows a very broad, rather weak band, with its maximum at 9.8 kK, mostly below the lower limit of the region studied by Brown, *et al.*, followed by a shoulder at 26.8 kK and a well-marked peak at 31.0 kK, which correspond closely to the bands reported at 27 and 31 kK by these authors.[13] Above this again we find two bands not previously reported: a well-defined shoulder at 38.8 kK and an intense peak at 48.0 kK. The latter absorption is readily assigned as an allowed charge-transfer, $\pi \rightarrow t_{2g}$, transition, on the basis of the known[28] optical electronegativity of Ru(IV) but the fitting of the d-d bands presents some difficulties. The band at 9.8 kK can reasonably be attributed to one or more spin-forbidden transitions, but low-spin d^4 systems always show a large number of closely juxtaposed spin-allowed, $t_{2g}{}^4 \rightarrow t_{2g}{}^3e_g$, bands at higher energies, thereby greatly complicating the band assignments. The most acceptable fit is provided by ascribing the broad weak band at 9.8 kK to a combination of three spin-forbidden bands, $^3T_{1g} \rightarrow {}^1T_{2g}$, ^1E_g, ^5E_g, and the features at 26.8, 31.0, and 38.8 kK to the groups of bands $^3T_{1g} \rightarrow {}^3E_g$, $^3T_{1g}$, $^3T_{2g}$; $^3T_{1g} \rightarrow {}^3A_{1g}$, $^3A_{2g}$, ^3E_g; and $^3T_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$, respectively. (Once again the spin-forbidden bands are relatively slightly more intense than in the first transition series.)

This results in calculated band positions which in some cases deviate quite appreciably from the experimental values but it is probable that at least the 38.8-kK shoulder appears at higher energy than the true band position by virtue of its proximity to the intense charge-transfer band. Some improvement in the fit could have been obtained by varying C/B, but for the reasons given above we did not wish to relax this constraint. (In fact, the fitting parameters are not strongly dependent on C/B, and our B is identical with that derived by Brown, *et al.*)

From the eigenvectors obtained by the diagonalization of the energy matrices, an estimate may be made of the extent of triplet character in the formally spin-forbidden transitions: for the $^1T_{2g}$ and ^1E_g ($t_{2g}{}^4$) levels the average value is slightly above 2%, and for the ^5E_g ($t_{2g}{}^3e_g$) state just over 1%. Consequently, relatively little of the observed intensity of the 9.8-kK band would be expected to derive from the ^5E_g level, but for the $^1T_{2g}$ and ^1E_g levels, which should again give rise to narrow bands, the observed relative intensities with respect to the spin-allowed excitations are of the correct order of magnitude. The F_R values observed for the 31.0- and 38.8-kK bands are rather high for d-d transitions, but both of them most probably represent more than one d-d excitation.

The d^5 hexafluororuthenate(III) anion, $RuF_6{}^{3-}$, shows[29] a magnetic moment of 1.25 BM, implying again a low-spin ($t_{2g}{}^5$, $^2T_{2g}$) ground state. In our spectrum the two expected spin-forbidden transitions, $^2T_{2g} \rightarrow {}^4T_{1g}$ and $^2T_{2g} \rightarrow {}^4T_{2g}$, appear as relatively weak bands at about 10.0 and at 15.4 kK. Although the first-order spin-orbit splittings of these bands are identical, diagonalization of the complete energy matrices indicates that the $^4T_{1g}$ be substantially more affected than the $^4T_{2g}$ state (see Table III), thereby supporting our assignment since the 10-kK band is broad and ill defined while the 15.4-kK absorption is a much narrower peak (*cf.* ref 8).

In the region of 4 kK there is some slight absorption but no clear indication of a lower energy band. The $^2T_{2g}$ ground state is split by spin-orbit coupling into a lower Γ_7 and an upper Γ_8 component, separated by $(^3/_2)\xi$ in the first order (diagonalization of the energy matrices gives 1.9 kK) so that a band would once more be expected between about 2 and 2.5 kK. It seems possible that the Ru(III) complex shows a rather smaller ξ than the Ru(IV) compound, so that the tail of such a band is not readily seen near 4 kK, whereas the Rh(IV) complex (qv), for which a larger ξ might be anticipated, gives a clear indication of the presence of the $^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$ band.

As for the d^4 system a low-spin d^5 ground state gives rise at higher energies to a considerable number of overlapping spin-allowed d-d bands, here $t_{2g}{}^5 \rightarrow t_{2g}{}^4e_g$ excitations. The sharp peak at 20.00 kK may be assigned quite readily to three closely grouped transitions, $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$, $^2T_{2g}$, but above this the absorption indicates the presence of bands corresponding to several transitions. The situation is not though quite as difficult as for $RuF_6{}^{2-}$ and a somewhat better fit is here possible by assigning the 26.5-kK shoulder as $^2T_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$, $^2T_{2g}$ and more tentatively the broad band at 34.0 kK as $^2T_{2g} \rightarrow {}^2A_{1g}$, ^2E_g. Above 40 kK the absorption increases rapidly, suggesting an intense band at about 55 kK (above our upper limit of 50 kK), which obviously represents a Laporte-allowed, $\pi \rightarrow t_{2g}$, charge-transfer excitation.

However, for the $RuF_6{}^{3-}$ anion the observed intensities correspond rather less well to the postulated assignments than do those of the d^3 and d^4 systems. For the $^4T_{1g}$ and $^4T_{2g}$ levels one calculates about 1.0-1.5% doublet character, *i.e.*, a comparable extent of allowed character as found for the spin-forbidden bands of $RuF_6{}^-$ and $RuF_6{}^{2-}$, but for low-spin d^5 systems both the spin-allowed and the spin-forbidden transitions represent $t_{2g}{}^5 \rightarrow t_{2g}{}^4e_g$ excitations. Consequently, the observed intensities of the spin-forbidden bands are appreciably greater than would be anticipated, relative to those of the spin-allowed bands. It is not at all clear why this should be so, although in the $5d^5$ system, $IrF_6{}^{2-}$, the spin-forbidden bands are also appreciably more intense relative to the spin-allowed transitions than is indicated by the eigenvectors from the matrix diagonalization.[8] The broad band at 34.0 kK is also a good deal more intense than the other two bands assigned as spin-allowed d-d excitations and its origin is therefore less certain; we were though reluctant to attribute this absorption to a charge-transfer transition since the known optical electronegativity of Ru(III) (*vide infra*) indicates that the lowest Laporte-allowed band would not be expected below about 55 kK, which corresponds very well with the steep increase in intensity just below 50 kK.

In addition to measuring the spectrum of the hitherto unstudied d^5 anion, $RuF_6{}^{3-}$, we have also reinvestigated that of the isoelectronic species, $RhF_6{}^{2-}$, this time using the cesium salt. As would be expected $RhF_6{}^{2-}$ also shows low-spin behavior, a magnetic moment of 1.7-1.9 BM being reported[30] for the Na salt, so that the ground state is again $^2T_{2g}(t_{2g}{}^5)$. For $RhF_6{}^{2-}$ Brown, *et al.*, reported[13] the two spin-forbidden bands at 12.2 and 16.1 kK, with spin-allowed transitions at 19-21 kK and at 26.0 kK, but no other absorptions below 40 kK were noted. Our spectrum broadly mirrors these findings but is better resolved in the 19-21-kK region and reveals additional absorptions at 32.8, 39.6, and 44.6 kK, together with a strong indication of a band below 4 kK.

As for $RuF_6{}^{3-}$ the $^2T_{2g}$ ground state will be split by spin-orbit coupling into Γ_7 and Γ_8 components, but a rather

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(28) C. K. Jorgensen, *Struct. Bonding (Berlin)*, 1, 3 (1966).

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(30) R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.*, 3579 (1952).

larger ξ might be expected for Rh(IV) than for Ru(III) so that the $^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$ transition would lie at rather higher energies, probably between 2 and 3 kK following the reasoning advanced for RuF_6^{2-}. (Note that in Tables I-IV the calculated figures have been derived using $\xi = 1000$ cm^{-1} for all the anions, because of the uncertainty over the values appropriate for each complex.) Consequently, the tail of this band is likely to be observable near 4 kK and we therefore adopt this assignment.

Our spectrum shows the two spin-forbidden bands, $^2T_{2g} \rightarrow {}^4T_{1g}$ and $^2T_{2g} \rightarrow {}^4T_{2g}$, at 11.6 and 16.0 kK, and as for RuF_6^{3-} (qv) this assignment is supported by the fact that the lower band is rather broad while the higher appears as a sharp inflection on the side of the nearby spin-allowed band (*cf.* calculated spin–orbit splittings, Table IV). The two spin-forbidden transitions are calculated to contain some 1.5–2.0% of allowed (doublet) character, so that as for RuF_6^{3-} the spin-forbidden bands appear to be more intense than would be expected, relative to the spin-allowed transitions, although the discrepancy is not quite so great. Again there is no obvious reason for this, but quantitative deductions from reflectance data are always handicapped by lack of information regarding the scattering coefficient and its frequency dependence.

In the 19-21-kK region we resolve two peaks, at 19.2 and 21.2 kK, which we assign as $^2T_{2g} \rightarrow {}^2T_{1g}, {}^2A_{2g}$ and $^2T_{2g} \rightarrow {}^2T_{2g}, {}^2E_g$, respectively, and at higher energy we find a shoulder at 27.6 kK, corresponding to the band of Brown, *et al.*, at 26 kK, followed by a new shoulder at 32.8 kK. As for RuF_6^{3-} the extensive band overlapping of the low-spin d^5 system causes difficulties in the fitting, but the most satisfactory result was obtained by assigning the 27.6- and 32.8-kK shoulders as $^2T_{2g} \rightarrow {}^2T_{1g}, {}^2T_{2g}, {}^2A_{1g}$ and $^2T_{2g} \rightarrow {}^2E_g$, respectively. The intensity of the 32.8-kK band is rather high for a d–d band but is probably due to the intense absorptions nearby at 39.6 and 44.6 kK, although possible contributions from a Laporte-forbidden, g → g type charge-transfer transition cannot be excluded. The stronger bands at 39.6 and 44.6 kK are though clearly Laporte-allowed charge-transfer excitations, and this is consistent with the known optical electronegativity of Rh(IV) which implies that these bands will begin just below 40 kK.

In addition to the work on the four compounds described above we also measured the spectrum of cesium hexafluoropalladate(IV); our results were essentially the same as those of Brown, *et al.*,[13] for this complex, but as expected from the χ_{opt} of this d^6 system no charge-transfer bands were discovered below 50 kK. The fitting parameters, $Dq = 2600$ cm^{-1} and $B = 400$ cm^{-1}, quoted by these authors differ from those adopted by Jorgensen,[31] who gives $Dq = 2590$ cm^{-1} and $B = 340$ cm^{-1}, but the former leads to a more reasonable value of β, the nephelauxetic ratio, in relation to that found[2] for NiF_6^{2-}, the difference probably arising from the use of different C/B ratios.

Using the values of the fitting parameters listed in Tables I-IV, the nephelauxetic ratios were calculated for the anions RuF_6^-, RuF_6^{2-}, RuF_6^{3-}, and RhF_6^{2-}, the required free ion values being derived according to the Jorgensen–Racah relationship.[31] These are given in Table V along with other values for 4d hexafluoro complexes taken from the literature. It will be seen that as in the first transition series the values of β ($=B_{complex}/B_{free\ ion}$) decrease progressively from left to right, representing the increased covalent contributions to bonding toward the end of the series, and the decreasing stabilities of the higher oxidation states. This behavior parallels that found[5,6] in the 3d series, and indicated[7,8] in the 5d block, but it is also interesting to note that for a given oxidation state of corresponding elements the nephelauxetic ratios increase from the first to the third transition series, thus reflecting the well-known increasing stability of the higher oxidation states (*cf.* ref 6).

Table V. Nephelauxetic Ratios for 4d Hexafluoro Anions

	Mo	Tc	Ru	Rh	Pd	Ag
MF_6^{3-}	0.90[a]		0.80[d]	0.64[e]		0.61[g] (0.48)[h]
MF_6^{2-}		0.75[b]	0.68[d]	0.54[d]	0.50[d,f]	
MF_6^{1-}		0.70[c]	0.55[d]			

[a] Reference 9. [b] Reference 11. [c] Reference 12. [d] Present work. [e] Reference 10. [f] Reference 13. [g] Reference 4. [h] β_{33} value.

Table VI. Interpretation of the Nephelauxetic Effect for Hexafluoro Anions of the 4d Series

	B, cm^{-1}	β	z_{min}	a^2_{min}	z_{root}	a^2_{root}	Ref
RuF_6^{3-}	550	0.80	1.25	0.89	1.9	0.95	*a*
RuF_6^{2-}	500	0.68	0.9	0.82	1.8	0.91	*a*
RuF_6^-	425	0.55	0.6	0.74	1.45	0.86	*a*
RhF_6^{2-}	410	0.54	0.4	0.73	1.1	0.86	*a*
PdF_6^{2-}	400	0.50	0.25	0.71	0.95	0.84	*a, b*
TcF_6^-	520	0.70	1.2	0.84	2.4	0.91	*c*

[a] Present work. [b] Reference 13. [c] Reference 12.

From the values of the nephelauxetic ratios it is possible to make semiquantitative estimates of the extent of covalency in the various complexes, using the method suggested by Jorgensen[32] and previously employed by us.[6] These results are shown in Table VI in which the values z_{min} and a^2_{min} represent respectively the effective charge on the metal assuming 100% of central-field covalency and the weighting coefficient of the metal atom wave function assuming 100% symmetry-restricted covalency. The values z_{root} and a^2_{root} represent the effective metal charge and metal atom weighting coefficient obtained by ascribing $\beta^{1/2}$ each to central-field and symmetry-restricted covalency, which Jorgensen suggests[32] as a realistic compromise. In Table VI are given the results derived from the present work, and from the data of Hugill and Peacock[12] for TcF_6^-, values for MoF_6^{3-}, RhF_6^{3-}, AgF_6^{3-}, and TcF_6^{2-} having been listed by us earlier.[6]

As for the MF_6^{3-} and MF_6^{2-} anions of the 3d series,[5] the positions of the charge-transfer bands for the corresponding complexes of the 4d series can readily be interpreted in terms of the spin-pairing energy treatment of Jorgensen,[33] who showed that the $\pi \rightarrow t_{2g}$ and $\pi \rightarrow e_g$ transitions could be accommodated by expressions of the form

$$E(\pi \rightarrow t_{2g}) = V + kD + q(A - E)$$

and

$$E(\pi \rightarrow e_g) = V + k'D + q(A - E) + \Delta$$

where k and k' depend upon the d^q configuration under consideration,[5] D is the spin-pairing energy, and V, A, and E have the significance previously explained.[5]

For the MF_6^{2-} anions of the 4d series, the positions of the t_{2g} bands are known accurately for the RuF_6^{2-} and RhF_6^{2-} complexes from the present work. For the two other known MF_6^{2-} anions, TcF_6^{2-} and PdF_6^{2-}, the first $\pi \rightarrow t_{2g}$ or $\pi \rightarrow e_g$ transition lies above 50 kK, the top limit of most spectrophotometers, but optical electronegativity data indicate that

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

(32) C. K. Jorgensen, *Progr. Inorg. Chem.*, 4, 73 (1962).

(33) C. K. Jorgensen, *Mol. Phys.*, 2, 309 (1959).

Table VII. Calculated Positions of Charge-Transfer Bands in 4d Hexafluoro Complexes

	B, cm^{-1}	C/B	D, kK	E, kK		Ref
				Calcd	Obsd	
MoF_6^{3-}	570	4.5	4.7	73	(71)	*a*
RuF_6^{3-}	550	4.75	4.7	51	55	*b*
RhF_6^{3-}	460	4.8	3.9	57[d]	(65)[d]	*a*
AgF_6^{3-}	470	5.0	4.1	43[d]	38[d]	*c*
TcF_6^{2-}	530	4.6	4.4	56	(55)	*a*
RuF_6^{2-}	500	4.75	4.2	48	48	*b*
RhF_6^{2-}	410	4.9	3.5	41	40	*b*
PdF_6^{2-}	400	5.0	3.5	56[d]	(55)[d]	*a*

[a] Estimated from MCl_6^{n-} data, ref 28. [b] Present work. [c] Reference 4. [d] These are $\pi \rightarrow e_g$ transitions; others are $\pi \rightarrow t_{2g}$ bands. Figures in parentheses estimated from data for corresponding hexachloro anions.

Table VIII. Optical Electronegativities for 4d Oxidation States

State	Mo	Tc	Ru	Rh	Pd	Ag
III	(1.7)		2.15[b] (2.05)[a]	(2.3)[a]		3.3[c]
IV		(2.2)[a]	2.5[b] (2.4)[a]	2.65[b] (2.6)[a]	(2.7)[a]	
V			2.8[b]			

[a] Reference 7 and sources cited therein. [b] Present work. [c] Reference 4.

for the MF_6^{n-} species the transition will generally be found at about 26 kK higher than for the corresponding MCl_6^{n-} species. Consequently, using the data listed by Jorgensen[28] the $\pi \rightarrow t_{2g}$ band of TcF_6^{2-} and the $\pi \rightarrow e_g$ band of PdF_6^{2-} should both be found near 55 kK, and the series may be fitted accurately by the values $V = 63$ kK, $D = 4$ kK, and $(E - A) = 5$ kK. The value of D is not, of course, strictly constant but varies only slightly within the series.

For the MF_6^{3-} series only the position of the $\pi \rightarrow e_g$ band for AgF_6^{3-} is known accurately.[4] Following our earlier reasoning[5] concerning the position of this band for CuF_6^{3-}, it is most probably located at 37.5 kK for the silver complex. For RuF_6^{3-} our present data indicate the $\pi \rightarrow t_{2g}$ band to be in the region of 55 kK, but for MoF_6^{3-} and RhF_6^{3-} the positions of the $\pi \rightarrow t_{2g}$ and $\pi \rightarrow e_g$ excitations, respectively, may only be estimated as before from the data for the hexachloro anions, the appropriate values being 71 and 65 kK. In view of these uncertainties it is not surprising that the MF_6^{3-} data are fitted rather less well, a moderate correlation being afforded by the parameters $V = 92$ kK, $D = 4.5$ kK, and $(E - A) = 9$ kK. Again D varies slightly within the series and these values together with the observed (or estimated) and calculated band positions are collected in Table VII. The $(E - A)$ value is probably exaggerated by the inclusion of the $\pi \rightarrow e_g$, AgF_6^{3-}, value, and the slope of the χ_{opt} *vs.* q plot (qv) is similarly overestimated. It is likely that this is because the $\pi \rightarrow e_g$ values for d^8 systems involve $(E - A)$ quantities relating to e_g orbitals as well as to t_{2g} orbitals, the former being greater in magnitude.

From the positions of the lowest energy Laporte-allowed charge-transfer bands the optical electronegativities, χ_{opt}, of the various oxidation states may also be determined. The energies of the $\pi \rightarrow t_{2g}$, or $\pi \rightarrow e_g$, bands are corrected as before[5,6] for the change in spin-pairing energy accompanying the $d^q \rightarrow d^{q+1}$ transition (and for Δ for $\pi \rightarrow e_g$ bands) and χ_{opt} is evaluated from the relationship

$$\sigma_{cor} = (\chi_{opt}(X) - \chi_{opt}(M^{n+})) \times 30 \text{ kK}$$

where $\chi_{opt}(X)$ is the optical electronegativity of the ligand and $\chi_{opt}(M^{n+})$ that of the metal cation corresponding to the oxidation state of the complex. For F^- χ_{opt} is taken from the Pauling scale as 3.9.

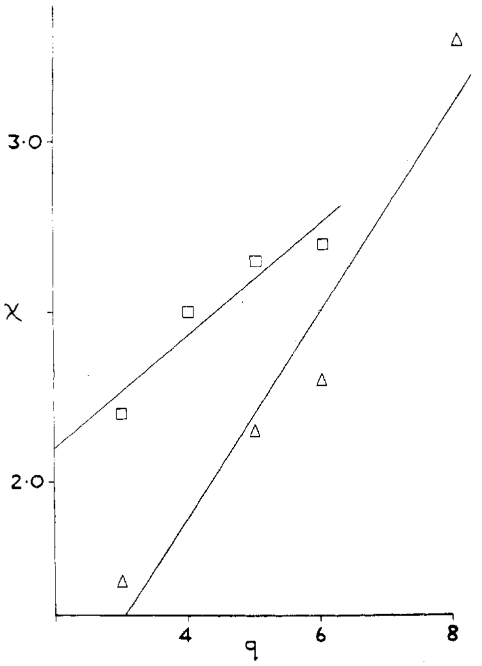

Figure 2. Correlation between χ_{opt} and q for 4d MF_6^{3-} and MF_6^{2-} anions: △, M(III); □, M(IV).

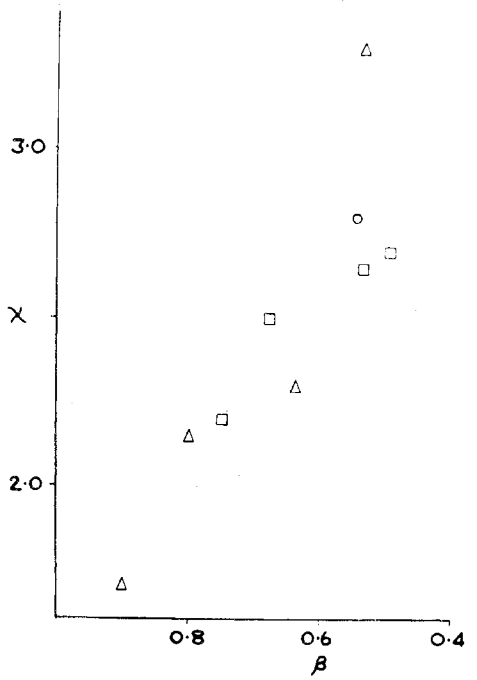

Figure 3. Relationship between χ_{opt} and β for 4d MF_6^{3-}, MF_6^{2-}, and MF_6^- anions: △, M(III); □, M(IV); ○, M(V).

The χ_{opt} values deduced for the hexafluoro anions here studied are shown in Table VIII, together with literature data for other metal oxidation states. The values shown in parentheses are derived from data for hexachloro species, and where χ_{opt} values were previously known those obtained from our data are in satisfactory agreement.

In conclusion, we note that as for the 3d series[5] the χ_{opt} values for a given oxidation state increase progressively from left to right across the 4d block, again reflecting the decreasing stability toward the end of the series, while the anticipated increase in χ_{opt} with oxidation state is also observed. Once more there exists the expected correlation between χ_{opt} and q, the occupation number, although the data for the M(III) states show considerably more scatter than that for M(IV) systems. The slopes of the $\chi_{\rm opt}$ *vs.* q plots are 0.313 (9.4 kK) and 0.165 unit (4.95 kK) which, as for the two 3d oxidation states,[5] are consistent with their interpretation[34] as $(E - A)$ (see Figure 2). We have moreover previously drawn attention[5,6] to the strong correlation which exists between optical electronegativity and the nephelauxetic ratio, and the theoretical basis for this.[14] A similar trend also occurs in the 4d series, as shown in Figure 3, and the data are thus consistent with the earlier results and the interpretation suggested.[5,6,14]

Registry No. KRuF$_6$, 40902-32-7; K$_2$RuF$_6$, 40902-49-6; K$_3$RuF$_6$, 40902-50-9; Cs$_2$RhF$_6$, 16962-25-7.

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Raman Spectra of Fluoro Fluorosulfuryl Peroxide and Trifluoromethyl Fluorosulfuryl Peroxide

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The liquid-phase Raman spectra of FOOSO$_2$F and CF$_3$OOSO$_2$F are reported in the region 2000–0 cm^{-1}. The infrared spectra are also reinvestigated in the region 2000–400 cm^{-1} for the gaseous compounds. Vibrational analyses are made for both molecules based on a description of the normal modes of vibration by the characteristic group vibrations. The O–O stretching vibrations are observed at 890 and 863 cm^{-1} for FOOSO$_2$F and CF$_3$OOSO$_2$F, respectively.

Introduction

The thorough study of the vibrational spectrum of CF$_3$OOCF$_3$ by Durig and Wertz[2a] has shown that Raman spectroscopy is a powerful tool in elucidating the O-O stretching frequency and thus the identification of the peroxy linkage in peroxides. While the O-O stretching vibration often gives rise to a weak absorption band in the infrared spectrum, it is usually the most intense band and is highly polarized in the Raman spectrum.

Relatively few inorganic peroxides are known and many of these have not been characterized spectroscopically. While hydrogen peroxide has been examined in detail, extensive vibrational spectral studies are limited to the symmetrical fluorinated peroxides CF$_3$OOCF$_3$,[2a] FSO$_2$OOSO$_2$F,[2b] and FOOF.[3] The O-O stretching frequency has been identified by Fox, *et al.*,[4] in a number of fluorinated peroxides, by Christe in a vibrational study of dimethyl peroxides,[5] by Aubke and coworkers in a study of the vibrational spectra of bis(fluorosulfuryl) peroxide,[2b] and by us in a vibrational study of bis(pentafluorosulfur) peroxide and fluorosulfuryl pentafluorosulfur peroxide.[6] Virtually no spectroscopic or structural information is available for the mixed, nonsymmetrical derivatives of these peroxides.

This study reports the Raman spectra of the unsymmetrical fluorinated peroxides FOOSO$_2$F and CF$_3$OOSO$_2$F. Only brief reports of their gaseous infrared spectra in the sodium chloride region have appeared.[7,8] A comparison of the two related molecules has provided a basis for detailed vibrational analyses.

Experimental Section

Fluoro fluorosulfuryl peroxide was prepared by the reaction of OF$_2$ and SO$_3$ (Allied Chemical Co.)[7] and purified by trap-to-trap distillation. Trifluoromethyl fluorosulfuryl peroxide was prepared by the reaction of CsOCF$_3$ and S$_2$O$_6$F$_2$.[9] S$_2$O$_6$F$_2$ was synthesized by catalytic fluorination of SO$_3$,[10] while CsOCF$_3$ was prepared by the reaction of CsF and COF$_2$ in the presence of acetonitrile.[11] Fractionation of the products yielded large amounts of CF$_3$OOSO$_2$F, contaminated with unreacted S$_2$O$_6$F$_2$. The purification of CF$_3$OOSO$_2$F was accomplished by the addition of elemental iodine, which converted the S$_2$O$_6$F$_2$ to the nonvolatile I(OSO$_2$F)$_3$, followed by trap-to-trap distillation.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer using a 10-cm gas cell fitted with potassium bromide cell windows (Harshaw Chemicals).

The Raman spectra were measured with a Jarrell Ash 25-300 Raman spectrometer using a Spectra-Physics 250 helium–neon laser for excitation at 6328 Å. The scattered radiation was detected at right angles to the incident beam (transverse viewing axial excitation) by means of a thermoelectrically cooled S-20 photomultiplier tube and photon counting system. Both FOOSO$_2$F (bp 0°) and CF$_3$OOSO$_2$F (bp 12°) were contained as liquids in 5-mm o.d. "optically flat" Pyrex cells at room temperature.

The spectrometer was calibrated from helium–neon plasma emission lines, and the accuracy is estimated to be ±1 cm^{-1}. Depolarization measurements were made by turning the direction of the electric vector of the incident light through 90° by means of a 45° rotation of a half-wave plate. Intensity values were obtained by measuring the area under the peaks.

Results

The Raman spectra of FOOSO$_2$F and CF$_3$OOSO$_2$F as obtained under instrumental conditions of low sensitivity are shown in Figure 1. The observed frequencies, relative intensities, and depolarization ratios are tabulated in Tables I and II for FOOSO$_2$F and CF$_3$OOSO$_2$F, respectively. The gas-phase infrared spectra are given for the region 2000–400 cm^{-1} and were found to be in excellent agreement with the

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