Electron Spin Resonance and Raman Spectra of $[ReOF_5]^-$ and Related Species in Aqueous Hydrofluoric Acid

By **John H. Holloway** * and **J. Barrie Raynor**,* Department of Chemistry, The University, Leicester LE1 7RH

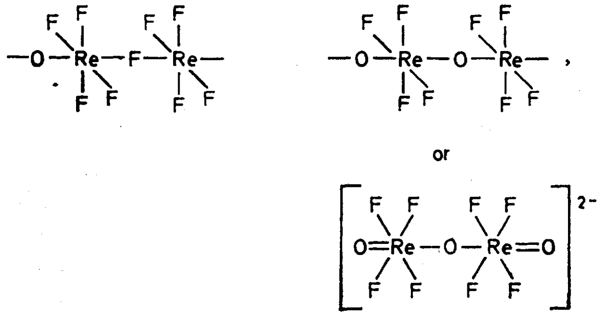
Raman spectra and electron spin resonance measurements on the products of partial hydrolysis of rhenium hexafluoride in aqueous hydrofluoric acid show that the main species is green $[ReOF_5]^-$. Assignments of the observed fundamental frequencies from the Raman spectra are as follows: 1008 (ν_1), 736 (ν_2), 700 (ν_8), 590 (ν_5), 575 (ν_3), 387 (ν_{10}), 370 (ν_7), 330 (ν_4), 298 (ν_9), and 233 (ν_6) cm^{-1} which confirms the expected C_{4v} symmetry. The e.s.r. parameters are: $g_{\parallel} = 1{\cdot}72$, $g_{\perp} = 1{\cdot}74$, $A_{\parallel}$ (Re) = 0·0960 cm^{-1}, $A_{\perp}$ (Re) = 0·0500 cm^{-1}, and $|Q'| = 0{\cdot}0045$ cm^{-1}, together with fluorine hyperfine coupling. The bonding parameters are $\beta_1 = 0{\cdot}78$, $\beta_2 = 0{\cdot}85$, and $\varepsilon = 0{\cdot}92$ showing considerable covalency. A transient blue species is considered to be an oxygen- or fluorine-bridged polymer.

RHENIUM HEXAFLUORIDE dissolves quite readily in anhydrous hydrogen fluoride to give a colourless solution. The introduction of traces of water result in the solution becoming pale blue. When slightly larger amounts of water are introduced the blue colour is only transient and after a few minutes the solution turns green.

In an investigation by Ippolitov [1] in 1962, the partial hydrolysis of octafluororhenates gave blue solids which were separated and characterized as salts of general formula $M[ReOF_5]$ (M = K, Rb, or Cs) on the basis of chemical analysis, magnetic measurements, and Noddak valency determinations. Solutions in organic solvents were said to remain blue for several hours but those in water turned green after a few minutes.

We have been unable to reproduce part of the Russian work. In particular, the colour changes described in the various modes of hydrolysis of the potassium salt do not occur in our samples, nor do any of the resulting solutions yield e.s.r. signals. Whilst our results do not rule out the possibility that $[ReOF_5]^-$ salts are blue, the reported ready solubility [1] of the salts in ethyl methyl ketone and the fact that $ReOF_4$ itself is blue suggest the possibility that the hydrolysis of M_2ReF_8 may in fact give rise to $ReOF_4$ and KF.

Our Raman and e.s.r. measurements confirm earlier Raman work [2] which suggested that ReF_6 in anhydrous HF is very little distorted from the octahedral configuration found in the gas phase,[3] there being little interaction with the solvent, and Raman, e.s.r., and optical spectra have shown that the green solutions contain monomeric $[ReOF_5]^-$. We propose that the transient blue colour is due to the formation of polymeric intermediates such as



EXPERIMENTAL

Pure rhenium hexafluoride was obtained by direct fluorination of rhenium metal with high purity fluorine. The reaction was carried out in a closed nickel reactor at 6 atm and 300 °C. To avoid contamination of the sample with ReF_7 a small excess of rhenium metal was used.[4] After purification by trap-to-trap sublimation, the absence of ReF_7 was verified by the complete absence of bands at 300 and 355 cm^{-1} in the i.r. spectrum.[5] Potassium octafluororhenate was prepared by direct reaction of ReF_6 with the stoicheiometric amount of potassium fluoride under pressure.

Samples were prepared for the various spectroscopic measurements by condensing ReF_6 onto purified anhydrous HF (specific conductivity $\approx 1 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$) in carefully dried, preseasoned Kel-F (polytrifluorochloroethylene) tubes and cells, and then allowing the ReF_6 to dissolve slowly as the mixture was allowed to warm to room temperature. The blue and green oxygen-containing solutions were obtained by condensing varying small amounts of water on to the refrozen ReF_6–HF solutions and allowing these to warm once again to room temperature.

Raman spectra were measured on a Coderg PH1 instrument with 488·0 nm excitation. U.v. measurements were made using a Unicam SP 700 spectrophotometer. E.s.r. spectra were obtained on a Varian E-3 instrument with facilities for variable-temperature control.

RESULTS

Raman Spectra.—The Raman shifts for the colourless ReF_6–HF solution at room temperature are compared with previously reported values [2] and those of ReF_6 vapour [3] in Table 1.

We were unable to obtain unambiguous Raman spectra of the blue solution because of rapid conversion into the green solution in the laser beam. The spectrum of the green solution showed numerous shifts which are listed with their assignments in Table 1. Bands at 330, 575, 736, and 1008 cm^{-1} are polarised.

Optical Spectra.—The spectra of the blue solution exhibited three main features: a peak at 14 300 cm^{-1}, a shoulder at *ca.* 16 400 cm^{-1}, and a shoulder at *ca.* 29 000 cm^{-1}. It was not possible to measure extinction coefficients accurately but the relative intensities of the absorptions were about 1·25 : 1·0 : 2·5.

The spectra of the green solution was significantly different and consisted of a peak at 14 000 cm^{-1}, a shoulder at *ca.* 19 700 cm^{-1}, and a peak at 25 500 cm^{-1}. Beyond this there were intense charge-transfer absorptions. The relative

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[1] E. G. Ippolitov, *Russ. J. Inorg. Chem.*, 1962, **7**, 485.

[2] B. Frlec and H. H. Hyman, *Inorg. Chem.*, 1967, **6**, 1596.

[3] H. H. Claassen, G. L. Goodman, J. H. Holloway, and H. Selig, *J. Chem. Phys.*, 1970, **53**, 341.

[4] J. G. Malm and H. Selig, *J. Inorg. Nuclear Chem.*, 1961, **20**, 189.

[5] B. Weinstock and J. G. Malm, *J. Inorg. Nuclear Chem.*, 1956, **2**, 380.

intensities of the main absorptions were similar to those of the blue solution.

E.s.r. Spectra.—The colourless ReF_6 solution in anhydrous HF exhibited no e.s.r. spectrum at 77 K as expected for a molecule of such high symmetry.

The blue solution gave no signal at room temperature and a broad line around 1500 G at 77 K. Upon addition of a trace of water, the spectrum of the green solution was superimposed upon the broad line.

TABLE 1

Raman bands (in cm^{-1}) and their assignments for ReF_6, $ReOF_5$, and $[ReOF_5]^-$

		Assignments		ReF_6		
$ReOF_5$ [c]	$[ReOF_5]^-$ (This work)	C_{4v}	O_h	Gas [b]	Ref. *a*	This work
125vw		$\nu_{11}(e)$	$\nu_6(t_{2u})$	147 (calc)		
234vw	233s	$\nu_6(b_1)$				
260 IR	298s	$\nu_9(e)$	$\nu_4(t_{1u})$	257 (calc)		
309vw P	330m, sh P	$\nu_4(a_1)$				
334s	370w	$\nu_7(b_2)$	$\nu_5(t_{2g})$	247s	249vw	246m
367s	387s	$\nu_{10}(e)$				
640m P	575w P	$\nu_3(a_1)$	$\nu_2(e_g)$	588m	578vw	587vw
652m	590w	$\nu_5(b_1)$				
715 IR	~700w, sh	$\nu_8(e)$	$\nu_3(t_{1u})$	715 (calc)		
989·8s P	1008s P	$\nu_1(a_1)$				
737·6vs P	736vs P	$\nu_2(a_1)$	$\nu_1(a_1)$	753·7vs	757vs	756vs

[a] Ref. 2. [b] Ref. 3. [c] Ref. 7. P Polarised band. IR Observed only in the i.r. spectrum.

No spectrum for the green solution was observed at room temperature, but as the temperature was lowered six broad lines appeared, which were narrowest (*ca.* 350 G wide) at *ca.* 175 K. These were attributed to hyperfine coupling to the rhenium. The field positions of the lines were as follows: *ca.* 1500, 2060, 2730, 3475, 4475, and 5670 G and the hyperfine coupling, after correction to second order,[6] was calculated to be 734 G with $g_{av} = 1{\cdot}800$. The line at lowest field was obscured by an absorption at *ca.* 1500 G which could possibly be attributed to a $\Delta_{m_s} = 2$ transition of residual blue species.

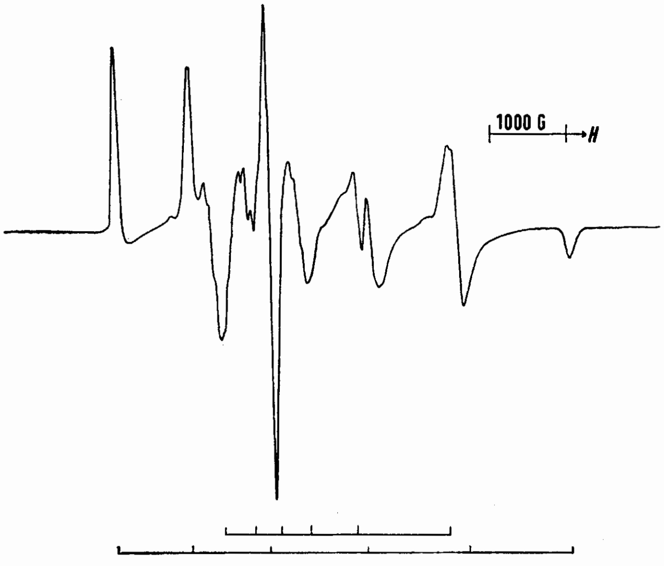

FIGURE 1 E.s.r. spectrum of the green solution at 77 K

At 77 K, a complex spectrum was obtained (Figure 1) which was analysed in terms of an axially symmetrical system. Six well-resolved parallel features were observed at field positions between 738 and 6665 G and corresponding perpendicular features between 2135 and 5060 G. The analysis of the spectrum was aided by a computer simulation which yielded the following parameters: $A_{\parallel}$ (Re) = $0{\cdot}0960$ cm^{-1}, $A_{\perp}$ (Re) = $0{\cdot}0500$ cm^{-1}, $g_{\parallel} = 1{\cdot}72$, $g_{\perp} = 1{\cdot}74$, $|Q'| = 0{\cdot}0045$ cm^{-1}. Although rhenium has two nuclei with nuclear spin (^{185}Re, 37·07%, $\mu_N = 3{\cdot}143$ nm, $I = 5/2$; ^{187}Re, 62·93%, $\mu_N = 3{\cdot}1760$ nm, $I = 5/2$), signals from the two isotopes were never resolved.

Under higher resolution numerous additional lines and shoulders appeared and were attributed to superhyperfine coupling to fluorine atoms. On the lowest-field rhenium parallel feature, the second-derivative spectrum clearly showed a multiplet of five equally spaced lines with a separation of 33 G and relative intensities *ca.* 1 : 4 : 6 : 4 : 1. We assign these features to interaction with four equivalent equatoral fluorine atoms. There was no evidence of further interaction with an axial fluorine atom, thus indicating that such coupling, if any, was small. The lowest-field rhenium perpendicular feature also exhibited fairly well resolved superhyperfine structure showing five features with an approximately equal spacing of 45 G. The relative intensities and spacings were slightly distorted because of the general shape of perpendicular features of a powder spectrum.

DISCUSSION

The Colourless ReF_6 *in* HF.—The three vibrations (Table 1) are readily assigned to the ν_1, ν_2, and ν_5 fundamentals in O_h symmetry since these are the only Raman-active modes. The close similarity between the gas-phase and solution spectra is strong evidence that the molecular structure in solution is similar to that in the gas phase, *viz.* discrete molecules. Our spectra are better resolved than those previously published.[2]

The Green Solution.—*Raman spectra.* The assignment of the Raman shifts was aided by the published assignments for $ReOF_5$ [7] and ReF_6.[3] The main problem was to decide whether the species in solution was $ReOF_4$ or $[ReOF_5]^-$. Table 1 correlates the vibrational modes for ReF_6 and $ReOF_5$. Our observation that the bands at 330, 575, 736, and 1008 cm^{-1} are polarised allows us to assign them to the ν_4, ν_3, ν_2, and ν_1 fundamentals by comparison with the assignments for $ReOF_5$. Other bands

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[6] B. Bleaney, *Phil. Mag.*, 1951, **42**, (7), 441.

[7] J. H. Holloway, H. Selig, and H. Claassen, *J. Chem. Phys.*, 1971, **54**, 4305.

are assigned by analogy with $ReOF_5$ and ReF_6. Had the species in solution been $ReOF_4$, then the ν_3 and ν_{10} fundamentals of $[ReOF_5]^-$ would be absent. The unambiguous detection of four polarised bands confirms that the species is $[ReOF_5]^-$.

The e.s.r. g-tensor. By analogy with the corresponding chromium and molybdenum oxide pentafluoride anions, we assign the unpaired electron to a $b_2(d_{xy})$ orbital in C_{4v} symmetry. If we take the relative order of the molecular-orbital energy levels as that for other d^1 metal oxide halide complexes [8,9] then $b_2(d_{xy}) < e(d_{xy,yz}) < b_1(d_{x^2-y^2}) < a_1(d_{z^2})$. The co-ordinate scheme is given in Figure 2, where X, Y, and Z represent the molecular-axis scheme and x, y, and z the local-axis scheme at each fluoride, where the x axis is along each metal–ligand bond. θ And ϕ are spherical polar angles which relate the external magnetic-field vector H to the Z and Y axes respectively. The orbitals necessary for the following discussion are given below, where β_1, β_2, and ε are orbital coefficients.

$$\psi\beta_2 = \beta_2\psi(d_{xy}) - \beta_2'\psi_{L_y} \qquad (1)$$

$$\psi\beta_1 = \beta_1\psi(d_{x^2-y^2}) - \beta_1'\psi_{L_x} \qquad (2)$$

$$\psi\varepsilon = \varepsilon\psi(d_{xz,yz}) - \varepsilon'\psi_{L_z} \qquad (3)$$

ψ_{L_y} Represents the ligand p_y orbitals which can overlap with the d_{xy} orbital by in-plane π-bonding, ψ_{L_z} represents the ligand p_z orbitals associated with out-of-plane π-bonding and ψ_{L_x} represents the ligand p_x orbitals associated with the σ-bonding.

First-order perturbation theory predicts that $g_\parallel < g_\perp < 2$, and this is true for many d^1 oxide pentahalide ions. However, for some, notably those with chloride or bromide as the halide, $g_\perp$ and $g_\parallel$ are reversed. Manoharan and Rogers [10] have explained this in terms of a contribution to the g-tensor by a spin–orbit interaction with ligands having a large spin–orbit parameter. Our results follow the first-order predictions and are in line with those of other oxide pentafluorides (Table 2).

Optical spectra. The three weak absorptions at 14 000, 19 700, and 25 500 cm^{-1} are assigned to the three orbitally forbidden transitions which are expected to be weakly observed, namely $b_2 \rightarrow e$, $b_2 \rightarrow b_1$, and $b_2 \rightarrow a_1$ respectively. The magnitude of the energy of these transitions is reasonable by comparison with the careful assignments of Wentworth and Piper [8] on single crystals of $[VOCl_5]^{3-}$ using polarised light.

The rhenium hyperfine tensor. The signs of the experimental hyperfine couplings to rhenium are all taken to be negative since this is the only combination of signs which gives a negative isotropic hyperfine coupling, as almost always found for transition-metal ions, and a negative principal value of the anisotropic tensor, as expected for a b_2 ground state.[11] In atoms where suitable wavefunctions are available, values can be calculated for the expected hyperfine coupling assuming 100% occupancy of a $5d$ orbital. Such values are available for the $3d$ and $4d$ ions in many electronic configurations,[12] but for rhenium it is only known for the $5d^6$ configuration, ($^{185}Re^+$, $-154{\cdot}8$ G). Since the value increases considerably as electrons are removed, then our value of -307×10^{-4} cm^{-1} is entirely reasonable. Unfortunately, without a reliable value for rhenium in a d^1 configuration, we cannot estimate the electron population in the $5d_{xy}$ orbital by this method.[9]

The bonding parameters. In order to calculate the bonding coefficients of the molecular orbitals 1—3 using the measured e.s.r. parameters, we have followed the basic theory of the g- and metal hyperfine-tensors developed by Abragam and Pryce,[13] and used the expressions given by Manoharan and Rogers and followed their notation:

$$g_\parallel - 2{\cdot}0023 = -\left(2\frac{(2\lambda_M\beta_2\beta_1 - \lambda_L\beta_2'\beta_1')}{\Delta E(b_2 \rightarrow b_1)}\right)(2\beta_2\beta_1 - 2\beta_1\beta_2'S_{b_2} - 2\beta_2\beta_1'S_{b_1} - \beta_1'\beta_2') \qquad (4)$$

$$g_\perp - 2{\cdot}0023 = -\left(\frac{2\lambda_M\beta_2\varepsilon}{\Delta E(\beta_2 \rightarrow e)}\right)(\beta_2\varepsilon - \beta_2\varepsilon'S_e - \varepsilon\beta_2'S_{b_2}) \qquad (5)$$

$$-\frac{A}{P} = \kappa\beta_2^2 + \tfrac{4}{7}\beta_2^2 + 2{\cdot}0023 - g_\parallel + \tfrac{3}{7}(2{\cdot}0023 - g_\perp) + \left(\frac{6}{7}\frac{\lambda_M\beta_2\varepsilon}{\Delta E(\beta_2 \rightarrow e)}(\beta_2\varepsilon'S_e + \varepsilon\beta_2'S_{b_2})\right) + \left(2\frac{(2\lambda_M\beta_2\beta_1 - \lambda_L\beta_2'\beta_1')}{\Delta E(b_2 \rightarrow b_1)}\right)(2\beta_2\beta_1'S_{b_1} + 2\beta_1\beta_2'S_{b_2} + \beta_1'\beta_2') \qquad (6)$$

$$-\frac{B}{P} = \kappa\beta_2^2 - \tfrac{2}{7}\beta_2^2 + \tfrac{11}{14}(2{\cdot}0023 - g_\perp) + \frac{11}{7}\left(\frac{\lambda_M\beta_2\varepsilon}{\Delta E(b_2 \rightarrow e)}\right)(\beta_2\varepsilon'S_e + \varepsilon\beta_2'S_{b_2}) \qquad (7)$$

S_{b_2}, *etc.* are overlap integrals between the metal orbital and ligand orbitals of the same symmetry. We were unable to evaluate these since no proper radial wavefunctions for the higher ionic species of rhenium are available. We have used the values estimated by Manoharan and Rogers for $[MoOF_5]^{2-}$, namely $S_{b_2} = 0{\cdot}12$, $S_e = 0{\cdot}16$, $S_{b_1} = 0{\cdot}20$. It is unlikely they will be greatly different from this, and in any case Manoharan and Rogers have shown that changes of up to $\pm 0{\cdot}04$ make little significant difference to calculated bonding coefficients. The only other equations required are of the type

$$\beta_1^2 + \beta_1'^2 - 2\beta_1\beta_1'S_{b_1} = 1 \qquad (8)$$

which allows calculation of the orbital coefficient of the ligands (dashed). The spin–orbit coupling constant for fluorine, $\lambda_L = 272$ cm^{-1},[14] whilst that for rhenium is

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[8] R. A. D. Wentworth and T. S. Piper, *J. Chem. Phys.*, 1964, **41**, 3884.

[9] K. de Armond, B. R. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, **1965**, **42**, 1019.

[10] P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, 1968, **49**, 5510.

[11] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Radiochem.*, 1970, **13**, 135.

[12] B. A. Goodman and J. B. Raynor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3406.

[13] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, 1951, **A205**, 135; 1951, **A206**, 164.

[14] D. S. McClure, *J. Chem. Phys.*, 1949, **17**, 905.

taken as 4200 cm^{-1} based upon the known value for Re^{6+}. P Was taken as 0·046 cm^{-1}.[11]

We now have sufficient information to solve equations (4)—(7) for the bonding coefficients. However, the functional forms are complicated by the second-order terms in equations (4)—(7). Fortunately, these are relatively small and they can be approximated by an iterative procedure in which the second-order terms are initially ignored, the bonding coefficients calculated to first order, and these coefficients then used to approximate the second-order terms for the final calculation.

TABLE 2

g-Tensor and fluorine hyperfine couplings in various d^1 complexes (units × 10^{-4} cm^{-1} except where G = gauss)

	$[CrOF_4]^-$	$[CrOF_5]^{2-}$	$[MoOF_5]^{2-}$ sol.	$[MoOF_5]^{2-}$ crystal	$[WOF_5]^{2-}$	$[TiF_2]^+$ in CH_3OH	$[VOF_4]^{2-}$	$[ReOF_5]^-$
$g_{\parallel}$	1·959	1·959	1·874	1·874	1·555		1·944	1·764
$g_{\perp}$	1·968	1·968	1·911	1·911	1·685		1·988	1·816
$A_{iso}(eq)$	5·87	5·68	11·1			7 G		
A_x	−22·97	−22·97	−24·98	−20·1	−30·5		10 G	45G av
A_y	+36·75	+36·75	+50·51	+53·1	54·6			
A_z		−6·8	−4·4	+3·7	−16·3			−33 G
$A_{(az)}$		1·74	0					
Ref.	*a*	*a, d, f, g*	*a, e*	*a, g*	*g, b*	*c*	*h*	This work

[a] Ref. 10. [b] R. S. Abradakhmanov, N. S. Garif'yanov, and E. I. Semenova, *Zhur. Strukt. Khim.*, 1968, **9**, 453. [c] E. L. Waters and A. H. Maki, *Phys. Rev.*, 1962, **125**, 233. [d] N. S. Garif'yanov, *Doklady Phys. Chem.*, 1964, **155**, 249. [e] N. S. Garif'yanov, V. N. Fedotov, and N. S. Kucheryavenko, *Bull. Acad. Sci. U.S.S.R. Chem. Div.*, 1964, **4**, 689; D. I. Ryabchikov, I. N. Marov, Y. N. Dubrov, V. K. Belyaeva, and A. N. Ermakov, *Doklady Akad. Nauk. S.S.S.R.*, 1966, **169**, 1107; J. T. C. Van Kemenade, J. L. Verbeek, and P. R. Cornaz, *Rec. Trav. chim.*, 1966, **85**, 629. [f] S. L. Verbeek and P. F. Cornaz, *Rec. Trav. chim.*, 1967, **86**, 209. [g] J. T. C. Van Kemenade, *Rec. Trav. chim.*, 1970, **89**, 1100. [h] G. M. Larin, Y. U. Buslaev, M. E. Dyatkina, and I. V. Miroshnichenko, *Zhur. Strukt. Khim.*, 1969, **10**, 993.

Repetition of the procedure resulted in the following bonding coefficients:

$$\beta_1 = 0{\cdot}78 \qquad \beta_1' = 0{\cdot}80$$
$$\beta_2 = 0{\cdot}85 \qquad \beta_2' = 0{\cdot}64$$
$$\varepsilon = 0{\cdot}92 \qquad \varepsilon' = 0{\cdot}57$$

As a consequence of the various assumptions and approximations, these values will not be highly accurate but they should be of the correct order of magnitude. The most significant thing here is the virtually pure covalent π-bonding in the molecule. We will compare these values with related complexes later in this paper.

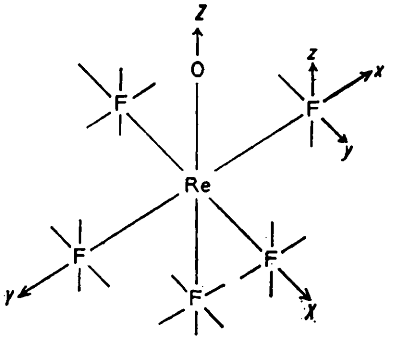

FIGURE 2 Axis notation for $[ReOF_5]^-$

Superhyperfine coupling to fluorine. Because of the difficulty of manipulating the solutions, we did not attempt to grow magnetically dilute single crystals. As a consequence, measurements were made on frozen solutions and our interpretation of the fluorine superhyperfine couplings is less certain than might otherwise have been the case.

The axial symmetry of the g-tensor shows that all four equatorial fluorine atoms are equivalent. The hyperfine tensor for each fluorine has to be considered in terms of the local symmetry axes as defined in Figure 2. The splitting of the rhenium parallel features in the spectrum into five equally spaced lines and appropriate intensity ratios confirms the equivalence of the four fluorines. The hyperfine coupling of 33 G is the z component of the experimental tensor. Determination of the separate x and y components is not possible directly since the superhyperfine coupling on the rhenium perpendicular features represents the average value $(x + y)/2$ as has been shown in certain square planar cupric complexes.[15] However, the average $(A_x + A_y + A_z)/3$ is A_{iso} and can be computed since $A_z = \pm 33$ G, $(A_x + A_y)/2 = \pm 45$ G; then the four possible combinations are:

(a) $A_z = +33$ G, $A_x + A_y = +90$ G, $A_{iso} = +41$ G

(b) $A_z = -33$ G, $A_x + A_y = +90$ G, $A_{iso} = +19$ G

(c) $A_z = -33$ G, $A_x + A_y = -90$ G, $A_{iso} = -41$ G

(d) $A_z = +33$ G, $A_x + A_y = -90$ G, $A_{iso} = -19$ G

It is difficult to decide which is more likely, but since known values of A_{iso} for other transition-metal d^1 fluorides do not exceed 11 G (Table 2), and that a positive value is expected,[8,16] then the value (+19) is the most probable and will be assumed in subsequent discussion. Since there will be positive spin density in the fluorine p_y orbital because of the direct overlap with the d_{xy} orbital, then the amount of this can be calculated directly from the bonding parameters. The total unpaired-electron density in all four p_y orbitals of the equatoral fluorines is given by the Mulliken population analysis to be equal to $(\beta_1^2)^2 - \beta_2\beta_2^1 S_{b_z}$.[16] For our case, it equals 0·34 or 8·5%

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[15] C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1969, 2229; J. B. Raynor, *Z. Naturforsch.*, 1969, **24b**, 775.

[16] R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.

in each p_y orbital, from which we can estimate the magnitude of the anisotropic tensor in the y direction. Since 100% occupancy of a p orbital on fluorine yields a splitting of +1085 G, then by proportion the tensor component A_{yy} would be +92 G.

TABLE 3

Bonding parameters for some complexes related to $[ReOF_5]^-$

	$[ReOF_5]^-$	$[VOCl_5]^{3-}$	$[VO(H_2O)_5]^{2+}$	$[CrOCl_5]^{2-}$	$[MoOF_5]^{2-}$	$[MoOCl_5]^{2-}$	$[MoOBr_5]^{2-}$
β_1	0·78	<1	0·981	0·592	0·891	0·754	0·596
β_2	0·85	⩽1	1	0·886	0·956	0·905	0·932
ε	0·92	0·992	0·962	0·958	0·960	0·901	0·844
Ref.	This work	*b*	*b*	*c*	*a*	*a*	*c*

[a] Ref. 10. [b] Ref. 9. [c] L. A. Dalton, R. D. Bereman, and C. H. Brubaker, *Inorg. Chem.*, 1969, **8**, 2477.

Since $A_z = -33$ G and $A_{iso} = +19$ G, then the tensor component $A_{zz} = A_z - A_{iso} = -52$ G. Also, $A_{yy} = +92$ G, therefore $A_{xx} = -40$ G. This tensor needs to be corrected for the dipolar interaction of the electron in the d_{xy} orbital by using the point-dipole approximation $A_{\text{dip}} = 2g_N\beta_N/r^3$ where r is taken as $1{\cdot}85 \times 10^{-10}$m as typical of a metal–fluorine bond length.[17] The principal value of the dipolar tensor is then +8 G and directed along the x axis. The corrected hyperfine tensor is now $A_{xx} = -48$ G, $A_{yy} = +96$ G, $A_{zz} = -48$ G. Unpaired electron density reaches the p_y orbital by direct in-plane π-bonding with the metal d_{xy} orbital. However, a different mechanism is needed to account for the anisotropic dipolar interaction in the p_x and p_z orbitals and also for the apparent spin density in the s orbitals of fluorine. The most likely explanation is *via* spin polarisation of the filled b_1 and e bonding molecular orbitals for the p_x and p_z orbitals (to yield negative spin density) and either *via* polarisation of the filled b_1 or by polarisation of the 2s and 2p_x fluorine orbitals by spin density in p_y which will lead to positive spin density in the 2s orbital.[8,15]

The axial fluorine. No interaction was observed with the axial fluorine. This is not surprising since there is no mechanism for direct delocalisation of electron density nor much chance of the spin-polarisation mechanism yielding hyperfine couplings large enough to be seen.

Comparison with other complexes. Table 3 lists the bonding parameters for some related complexes. The bonding in $[ReOF_5]^-$ is more covalent than in $[MoOF_5]^{2-}$ but rather similar to that in $[MoOCl_5]^{2-}$. This reflects the larger radial distribution of the d_{xy} orbital in Re and Cl compared with Mo and F. The most striking feature is the covalency of the σ-bond in $[ReOF_5]^-$.

Very few e.s.r. studies have been made on other d^1 rhenium complexes and none in sufficient detail to make meaningful comparisons.[18]

The Blue Solution.—The blue solution differs significantly from the green solution in exhibiting no resolved e.s.r. spectrum at 77 K and showing three optical absorptions at different energies. We have strong e.s.r. evidence that the green solution consists of monomeric $[ReOF_5]^-$ ions and propose that the blue solution contains polymeric $O{-}ReF_4{-}O{-}FeR_4^-$, $O{-}ReF_4{-}F{-}ReF_4^-$, or $[O{-}ReF_4{-}O{-}ReF_4{-}O]^{2-}$ units. The close proximity of the rhenium atoms would permit an antiferromagnetic interaction between the electrons and prevent observation of resolved e.s.r. spectrum at 77 K. Our observation of a possible $\Delta m_s = 2$ transition supports this. The optical spectra can now be explained if we say that the blue polymeric species has a larger axial distortion than the monomeric $[ReOF_5]^-$. The effect upon the energy levels is seen in Figure 3. Since the e and b_1 levels in $[ReOF_5]^-$ are relatively close (*ca.* 5000 cm^{-1}), then an increased axial distortion would increase the separation of the b_2 and e orbitals and also that of the b_1 and a_1 orbitals. The effect could be a reversal of the b and e energy levels in the blue species.

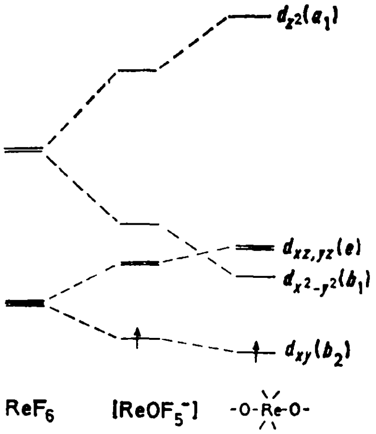

FIGURE 3 Order of the energy levels for ReF_6, $[ReOF_5]^-$, and —O—Re—O—

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