Electronic and Electron Paramagnetic Resonance Spectra and Metal–Ligand Bonding of VF_4†

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The electronic and EPR spectra of the tetragonally compressed VF_6^{2-} complex present in VF_4 have been recorded. Transitions to the levels derived from the ^2E_g state of the parent octahedral complex occur in the visible region, while those between components of the $^2T_{2g}$ ground state occur in the infrared region. Angular-overlap and molecular-orbital X_α calculations are presented and compared with previous results for other complexes.

The chemistry of vanadium(IV) is dominated by the numerous complexes formed by the VO^{2+} ion, though the tetrahalides are exceptions in this respect.[1] However, while VCl_4 and VBr_4 are monomeric, VF_4 is polymeric, and the recent report[2] of the determination of the crystal structure of the latter compound provides an opportunity to compare the spectroscopic and bonding properties of a six-co-ordinate vanadium(IV) compound with those of the four-co-ordinate tetrachlorovanadate and five-co-ordinate oxovanadium(IV) complexes. We report here the electronic absorption and EPR spectra of VF_4 and interpret these using the angular overlap model (AOM).[3] In addition, molecular-orbital X_α calculations are presented and compared with those recently reported[4] for VCl_4 and various oxovanadium(IV) complexes.

Experimental

The preparation of VF_4 as small green plates has already been described.[2] Since the compound hydrolyses readily, several crystals were mounted in quartz capillary tubes and the electronic absorption spectra in the visible region were measured using a Cary 17 spectrophotometer by a method described previously.[5] The samples were cooled using a Cryodyne 22C cryostat. The well developed crystal face was not pleochroic, and no difference was observed between the spectra recorded using polarised light with the electric vector along each extinction direction of this face. Spectra in the region 1600–4000 cm^{-1} were measured using a Digilab FTS-20E spectrometer fitted with an IRMA microscope attachment. The EPR spectra of a powdered sample in a sealed quartz tube were recorded at both X- and Q-band frequency at room temperature and ≈ -100 °C using a JEOL FE3X spectrometer; a similar spectrum was observed at each frequency, and at the two different temperatures. Attempts were also made to measure the EPR spectra of single crystals, but these were unsuccessful.

Results and Discussion

The metal ion in VF_4 lies on a crystallographic inversion centre, and forms two short terminal V–F bonds (169.6 pm) and four longer approximately equal bonds (191.8 and 192.3 pm) to fluorides which bridge to neighbouring metal ions.[2] Although the bridging V–F–V angles are 150.7°, each angle between the neighbouring axial and in-plane V–F bonds deviates from 90° by less than 1°, so that the local symmetry about the V^{4+} approximates well to the D_{4h} point group.

Electronic Spectrum.—The absorption spectrum of a typical crystal of VF_4 in the region 10 000–26 000 cm^{-1} at 15 K is shown in Fig. 1; the room-temperature spectrum was identical except that the bands were slightly more intense and less well resolved. In the region 10 000–12 000 cm^{-1} the spectrum was found to vary somewhat from one sample to another and the dashed line represents the average of those observed. The spectrum consists of a band centred at 15 000 cm^{-1} with a weaker peak at $\approx 23\,000$ cm^{-1} occurring as a pronounced shoulder on the intense absorption commencing at $\approx 26\,500$ cm^{-1} which is presumably due to the onset of ligand to metal charge-transfer transitions. In a compressed tetragonal ligand field produced by a π-donor like fluoride, the ^2E_g excited state of the parent octahedral complex is split into states of $^2B_{1g}(x^2 - y^2)$ and $^2A_g(z^2)$ symmetry, the latter being higher in energy. The bands at 15 000 and $\approx 23\,000$ cm^{-1} may therefore be assigned to transitions to these two states, respectively.

The splitting of the $^2T_{2g}$ ground state is expected to be $\approx 1/4$ that of the excited state,[3] *i.e.* ≈ 2000 cm^{-1}, with the $^2E_g(xz,yz)$ state being higher in energy. The spectrum in the region 1600–4000 cm^{-1} consists of a weak band centred at 3450 cm^{-1}, a cluster of weak, sharp peaks at ≈ 2900 cm^{-1}, and a pair of peaks at 2350 and 2470 cm^{-1}, with several weaker peaks occurring at lower energy. The band at 3450 cm^{-1} is tentatively assigned to the stretching vibration of traces of OH^-; bands due to charge-transfer transitions associated with small amounts of OH^- substituting for Cl^- have been identified in the single-crystal optical spectra of chlorocuprates.[6] The weak peaks at ≈ 2900 cm^{-1} are most likely due to the C–H stretching vibrations of the grease used to attach the crystal to the capillary, while the rising background at lower energy is due to the absorption of the quartz itself, as shown by a 'blank' spectrum. The peaks at 2350 and 2470 cm^{-1} are probably due to transitions to the $^2E_g(xz,yz)$ state, split by spin–orbit coupling and low-symmetry components of the ligand field. The only alternative assignment is to overtones of V–F stretching vibrations, but since these lie[7] below ≈ 1000 cm^{-1} this seems unlikely. The magnitude of the splitting, ≈ 120 cm^{-1}, is consistent with the spin–orbit splitting of the $^2E_g(xz,yz)$ state; a calculation using the ligand-field computer program CAMMAG[8] (see subsequent discussion)

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† *Supplementary data available* (No. SUP 56906, 2 pp.): orbital energies and electron populations. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

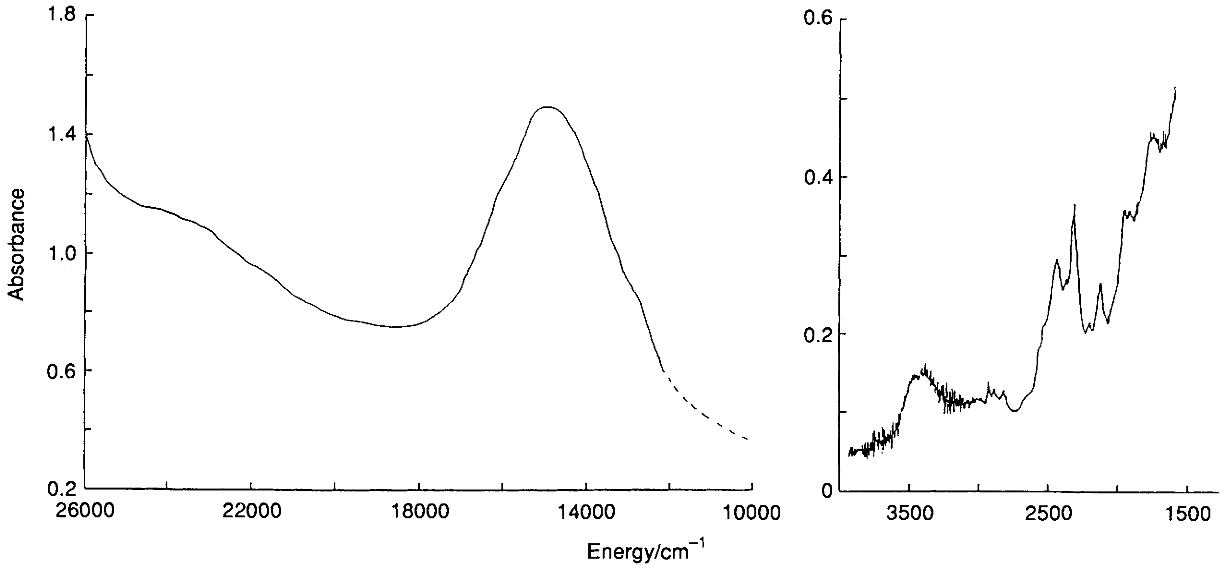

Fig. 1 Typical electronic absorption spectrum of an arbitrary crystal face of VF_4 measured at room temperature in the range 1600–4000 cm^{-1} and at ≈15 K in the region 10 000–26 000 cm^{-1}. The portion represented by a dashed line was somewhat irreproducible and represents the average of several spectra

yielded an estimate of 130 cm^{-1} for this splitting. The small widths of the bands at 2350 and 2470 cm^{-1} are also consistent with the above assignment, as the $^2E_g(xz,yz)$ excited state is only weakly antibonding.[5] A rather similar pattern was observed[9] in the electronic spectrum of the linear $[NiO_2]^{2-}$ complex, where the lower-energy transition to the $^3\Phi_g$ state produced a relatively sharp band, showing vibrational and spin–orbit fine structure even at room temperature, while the higher-energy $^3\Pi_g$ transition was broad and almost featureless. Conceivably the weaker peaks at 2145 and 1966 cm^{-1} may be due to 'hot' bands,[5] but as a low-temperature spectrum could not be measured in this region this could not be tested experimentally.

EPR Spectrum.—The powder EPR spectrum of VF_4 consists of a single, broad, symmetric resonance centred at $g = 1.93$ [peak-to-trough width of the first derivative ≈800 G (8×10^{-2} T)]. The two molecules in the unit cell of VF_4 have almost identical orientations,[2] so that even if electron exchange between these is rapid the observed spectrum effectively relates to the molecular g tensor.* To first order, the molecular g shifts from the free-electron value are related to the excited-state energies E by the expressions[10] (1) and (2). Substitution of the

$$\delta g_z = -8\lambda k_z^2/E(x^2 - y^2) \quad (1)$$

$$\delta g_{xy} = -2\lambda k_{xy}^2/E(xz,yz) \quad (2)$$

value $\lambda = 170$ cm^{-1} for the spin–orbit coupling constant in equations (1) and (2), corresponding to an effective nuclear charge of +2 for the vanadium ion in VF_4, as assumed in similar compounds,[11] together with the values of $E(x^2 - y^2)$ and $E(xz,yz)$ derived from the electronic spectrum, yields the values $g_z = 1.94$ and $g_{xy} = 1.92$ assuming orbital reduction parameters $k_z = k_{xy} = 0.85$. Similar results were obtained by exact calculation with $k_z = k_{xy} = 0.75$ using the computer program CAMMAG developed by Gerloch and co-workers[8] and the bonding parameters below. A computer simulation using these g values produced a spectrum in good agreement with that observed experimentally, the large linewidth meaning that the slight g anisotropy has no observable effect on the spectrum.

Metal–Ligand Bonding Parameters.—Within the framework of the AOM[3] the d-orbital energies E in a tetragonal complex are related to the σ- and π-bonding parameters of the axial and in-plane ligands, $e_\sigma(z)$,$e_\pi(z)$,$e_\sigma(xy)$,$e_\pi(xy)$ by expressions (3)–(6).

$$E(z^2) = 2e_\sigma(z) + e_\sigma(xy) \quad (3)$$

$$E(x^2 - y^2) = 3e_\sigma(xy) \quad (4)$$

$$E(xy) = 4e_\pi(xy) \quad (5)$$

$$E(xz,yz) = 2e_\pi(xy) + 2e_\pi(z) \quad (6)$$

The d-orbital splitting in a regular octahedral complex is given by $\Delta = 3e_\sigma - 4e_\pi$ so that the $^2B_{2g}(xy) \longrightarrow {}^2B_{1g}(x^2 - y^2)$ transition occurs at exactly Δ for the in-plane ligands. The value observed for VF_4, 15 000 cm^{-1}, is actually slightly smaller than that reported[12] for VF_6^{3-}, 16 100 cm^{-1}, though the average of the VF_4 transition energies, 19 000 cm^{-1} is reasonably close to the $^2T_{2g} \longrightarrow {}^2E_g$ transition energy of 20 250 cm^{-1} reported[13] for the regular VF_6^{2-} ion in K_2VF_6. The energy difference between the $^2B_{1g}(x^2 - y^2)$ and $^2A_g(z^2)$ states provides a measure of the greater σ-bonding power of the more closely bound axial fluorides compared with the in-plane ligands, and this difference is substantial, ≈8000 cm^{-1}.

Assuming that $e_\sigma \approx 4e_\pi$ for the in-plane ligands, as has been deduced for other complexes involving ligands such as fluoride,[14] the observed transition energies may be substituted in equations (3)–(6) to estimate the following bonding parameters (in cm^{-1}): $e_\sigma(z) = 11\,500$, $e_\pi(z) = 3075$, $e_\sigma(xy) = 7500$ and $e_\pi(xy) = 1875$. These suggest a Δ value of 22 200 cm^{-1} for the axial fluorides. The large difference compared with the value for the in-plane fluorides, 15 000 cm^{-1}, presumably reflects the difference in bond lengths (169.6 and 192 pm, respectively). Over short changes in bond length r it has been observed[15] that the ligand-field splitting varies as $\approx r^{-5}$. This would imply that the axial ligands should have a Δ value ≈85% larger than that of the in-plane ligands, rather than the ≈50% derived from the above analysis. It seems unlikely that the discrepancy is caused by the fact that the in-plane fluorides are bridging, rather than

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* The maximum and minimum values of the exchange-averaged crystal g tensor correspond to $0.93g_z + 0.07g_{xy}$ and g_{xy}.

terminal, ligands, as this should accentuate the difference in ligand-field strengths. A contributing factor may be that, in tetragonally distorted complexes such as VF_4, configuration interaction with the $^2A_g(4s)$ state will depress the energy of the $^2A_g(z^2)$ state, lowering the effective value of $e_\sigma(z)$. Such an effect is well established from analyses of the EPR[16] and optical spectra[17] of the analogous tetragonally compressed complex $[CuF_6]^{4-}$, but it seems unlikely that it plays a large role in VF_4 since the ratio derived for $e_\sigma:e_\pi \approx 3.7:1$ is quite close to the expected value of 4:1.

It is interesting to compare the energy levels in VF_4 with those in typical oxovanadium(IV) complexes. These generally have approximate C_{4v} symmetry with the transitions $^2B(xy) \longrightarrow {}^2E(xz,yz)$ and $^2B(x^2 - y^2)$ occurring at $\approx 13\,000$ and $\approx 16\,000$ cm^{-1}, respectively, and that to the $^2A(z^2)$ state lying at $\approx 23\,000$ cm^{-1} for five-co-ordinate complexes, but rising to $> 30\,000$ cm^{-1} when a ligand co-ordinates *trans* to the V=O oxygen atom.[18] Thus, the in-plane ligand field in oxovanadium(IV) complexes is very similar to that in VF_4, as is the axial field when this is produced solely by the single oxygen atom of the vanadyl group. On the other hand, the $^2E(xz,yz)$ excited state is much higher in energy in oxovanadium(IV) complexes, presumably reflecting the very strong π interaction associated with the V=O linkage. It is the high energy of the $^2E(xz,yz)$ excited state which causes the significant g anisotropy observed for oxovanadium(IV) complexes, which typically have $g_z \approx 1.93$ and $g_{xy} \approx 1.98$,[10] in marked contrast to the almost isotropic g tensor of VF_4.

Molecular-orbital Calculations.—Recently the discrete variational $X_\alpha(DVX_\alpha)$ model has been shown to provide a useful method of investigating the bonding in transition-metal complexes,[4,19] suggesting it would be of interest to apply this model to VF_4. The computational procedure described in detail previously[19] was therefore used to calculate the energy levels and associated wavefunctions in this compound, the detailed listing of the results being deposited as SUP 56906. The calculated energies (in cm^{-1} using Slater's transition-state formalism[20]) were found to be: $^2E_g(xz,yz)$ 2970 (2400), $^2B_1(x^2 - y^2)$ 19 656 (15 000) and $^2A_g(z^2)$ 30 073 ($\approx$23 000), the experimental values being in parentheses.

The splittings estimated for the $^2T_{2g}$ and ^2E_g states of the parent octahedral complex are in reasonable agreement with experiment, though the baricentre calculated for the $^2B_1(x^2 - y^2)$ and $^2A_g(z^2)$ states is ≈ 6000 cm^{-1} too high in energy, a considerably greater deviation than was observed when similar calculations were carried out on a range of oxovanadium(IV) complexes and the tetrahedral molecule VCl_4.[4] To test whether the discrepancy is due to the fact that VF_4 is a continuous lattice in two dimensions, calculations were also carried out using the 'embedded cluster' approximation.[21] Using the crystal structure coordinates, the potentials of all atoms within an 8.64 au (*ca.* 45.7×10^{-11} m) radius of the reference central V atom were explicitly included in the summation. The overall cluster size represents 37 atoms, V_5F_{32}, but the embedded-cluster calculation produced no significant change in the results. The $b_{2g}(xy)$ orbital containing the unpaired electron was calculated to have 83% d_{xy} and 17% ligand p character, while the higher-energy $a_g(z^2)$ orbital had 73% d_{z^2}, 2% metal 4s and 25% ligand p character, in good agreement with the orbital reduction parameter $k \approx 0.8$ estimated from the EPR spectrum. It is interesting that the composition of the latter orbital is quite similar to that deduced for the analogous orbital of the $[CuF_6]^{4-}$ ion present in Cu^{2+}-doped K_2ZnF_4 from the analysis of the hyperfine parameters (75.1% d_{z^2}, 2.6% metal 4s, 20.6% ligand p and 1.7% ligand s character).[16] This complex is thought to have a compressed tetragonal geometry similar to that in VF_4 (axial and equatorial Cu–F bond lengths estimated[22] as 189 and 210 pm) and in this case the 4s contribution to the $a_g(z^2)$ orbital can be measured relatively accurately from the isotropic contribution to the copper(II) hyperfine coupling constants.

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