# Metal–Ligand Bonding in some Vanadium Compounds: A Study based on *X*-Ray Emission Data

By **J. B. Jones** and **D. S. Urch,*** Chemistry Department, Queen Mary College, London E41 4NS

$K_\alpha$ And $K_\beta$ $X$-ray emission spectra of V (metal), [V(pd)$_3$] (pd = pentane-2,4-dionate), $VF_3$, $VO_2$, $V_2O_5$, [VO][SO$_4$], [NH$_4$][VO$_3$], and [NH$_4$][V$_3$O$_8$] are reported. It is argued that peaks of higher energy than $K_{\beta_{1,3}}$ are due to transitions involving molecular orbitals with V $p$ character rather than V $3d$. The relative intensities and emission energies of the $K_{\beta_{1,3}}$, $K_{\beta''}$, and $K_{\beta_{2,5}}$ peaks are discussed using m.o. theory. The $K_{\beta''}$ : $K_{\beta_{2,5}}$ relative intensity is much higher than for comparable main-group compounds; this is probably due to the presence of $3p$ character in the orbital that gives rise to $K_{\beta''}$; $3p$ character also enhances the intensity of $K_{\beta_{2,5}}$. Changes in peak positions and relative intensities associated with the oxidation state of vanadium can be qualitatively rationalised by a consideration of $4p$ character alone. It is suggested that the $K_{\beta'''}$ peak observed at higher energies (+15 eV) than $K_{\beta_{2,5}}$ is formed by relaxation of an electronically excited species (resonance radiation).

*X*-RAY emission spectra arise from electronic transitions to vacancies in inner orbitals. Since atomic selection rules operate, and in particular $\Delta l = \pm 1$, an $s$ vacancy will attract electrons only from $p$ orbitals, *etc.* Thus when valence-shell electrons are involved $X$-ray emission spectroscopy becomes a valuable technique for investigating not only the relative energies of the molecular orbitals but also the degree of participation of specific atomic orbitals in bond formation.[1] The bonding between second-row elements and ligands such as oxygen and fluorine has been investigated in this way.[2,3] The purpose of this paper is to attempt to extend the method to a study of the bonding in transition-metal compounds. Vanadium was chosen because the variety of valence states enables the effect of formal charge on $X$-ray emission frequencies to be determined and also because of the ready availability of a wide range of compounds.

The $X$-ray emission spectra of some vanadium compounds have already been reported. Fischer[4] studied a series of oxides, borides, nitrides, and carbides, whilst Romand *et al.*[5] made a detailed investigation of vanadium nitrides. Bonding in the vanadate anion, and also related oxo-anions of manganese and chromium, has been the subject of much theoretical calculation.[6-10] In some cases correlations with $X$-ray emission (*e.g.* Best [6] and Hillier and his co-workers [8]) or $X$-ray photoelectron spectra (*e.g.* Prins [10]) have also been attempted. The experimental results presented in this paper will, where possible, be compared with theoretical predictions; in other cases simple molecular-orbital (m.o.) theory will be used to provide a semiqualitative framework [2,3] for the discussion of the results. The spectra themselves were obtained using secondary excitation (*i.e.* $X$-ray fluorescence) since it has been shown that some chemical compounds are decomposed by direct electron bombardment.[11]

## NOMENCLATURE

A vacancy in the vanadium $1s$ orbital gives rise to $K_{\alpha_{1,2}}$ ($2p \rightarrow 1s$), $K_{\beta_{1,3}}$ ($3p \rightarrow 1s$), and higher-energy $K$ emission features variously designated $K_{\beta_2}$ ($4p \rightarrow 1s$) and $K_{\beta_5}$ ($3d \rightarrow 1s$) at energies of 4 949, 5 426, and 5 462 eV † and relative intensities approximately in the ratio $K_{\alpha_{1,2}} : K_{\beta_{1,3}} : K_{\beta_{2,5}} = 3\,000 : 400 : 1$.[12] That the high-energy peak should be designated $K_{\beta_5}$, corresponding to a dipole-forbidden transition, was first suggested by Idei [13] since the $4p$ orbitals would be empty in an isolated vanadium atom. However, the $X$-ray emission properties of isolated vanadium atoms have yet to be studied and, whether from vanadium metal or from a vanadium compound, the $X$-ray emission spectra that have been obtained have all been from materials with a complex m.o. bond structure in which $4p$ orbitals might play a part. Ligand-field theory [14] certainly assumes that $4p$ orbitals are involved in first-row transition-metal atom–ligand interactions. Whilst most authors have followed Idei's proposal, some have been more cautious; they refer to the high-energy peak in transition-metal $K$ emission spectra as $K_{\beta_{2,5}}$ (*e.g.* ref. 6).

In elements with atomic numbers greater than 31 (gallium) it is possible to observe $K_{\beta_2}$ and $K_{\beta_5}$ as distinct features. Invariably $K_{\beta_5}$ is very much weaker than an authentic $K_{\beta_2}$ peak (intensity ratio, $K_{\beta_5} : K_{\beta_2}$ *ca.* 1 : 20).[12] This would seem to suggest that for elements of atomic number *ca.* 30 the transition moment $\int \psi_{1s} P \psi_{4p}\, d\tau$ is very much greater than $\int \psi_{1s} P \psi_{3p}\, d\tau$ (where $P$ is the transition operator). If there is no drastic change in the ratio of these two integrals on going to lower atomic numbers (*i.e.* 30—22) then it is most reasonable to assume that the high-energy peaks in the $K$ emission spectrum arise from $p$ character in occupied m.o.s and that the intensity of peaks from the corresponding presence of $3d$ character in occupied m.o.s will be too weak to be observed. Since, however, the point cannot be unequivocally resolved by argument, the most prudent designation would seem to be $K_{\beta_{2,5}}$. Whatever their atomic origin, however, these $X$-ray

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† 1 eV ≈ $1.60 \times 10^{-19}$ J, 1 Torr = (101 325/760) Pa.

[1] D. S. Urch, *Quart. Rev.*, 1971, **25**, 343.

[2] D. S. Urch, *J. Phys. (C)*, 1970, **3**, 1275.

[3] D. S. Urch, *Adv. X-Ray Agalysis*, 1971, **14**, 250.

[4] D. W. Fischer, *J. Appl. Phys.*, 1970, **41**, 3561.

[5] M. Romand, J. S. Soloman, and W. L. Baun, *Spectrochim. Acta*, 1973, **B28**, 17.

[6] P. E. Best, *J. Chem. Phys.*, 1966, **44**, 3248.

[7] I. H. Hillier and V. R. Saunders, *Proc. Roy. Soc.*, 1970, **A320**, 161.

[8] J. A. Connor, I. H. Hillier, V. R. Saunders, M. H. Wood, and H. Barber, *Mol. Phys.*, 1972, **24**, 497.

[9] D. W. Clack, *J.C.S. Faraday II*, 1972, 1672.

[10] R. Prins, *J. Chem. Phys.*, 1974, **61**, 2580.

[11] D. W. Fischer and W. L. Baun, *Norelco Reporter*, 1967, **14**, 92; *Analyt. Chem.*, 1968, **37**, 902.

[12] E. W. White and G. G. Johnson, jun., '*X*-Ray Emission and Absorption Wavelengths and Two-theta Tables,' 2nd edn., Amer. Soc. for Testing and Materials, Philadelphia, 1970, ASTM data series DS 37A.

[13] S. Idei, *Nature*, 1929, **123**, 643.

[14] C. J. Ballhausen, 'Ligand Field Theory,' McGraw-Hill, New York, 1962.

emission peaks of higher energy than vanadium $K_{\beta 1,3}$ result from electronic transitions from valence-shell m.o.s and for this reason it is the $K_{\beta 2,5}$ region which is investigated in detail in this paper.

## EXPERIMENTAL

Apart from ammonium trivanadate, $[NH_4][V_3O_8]$, which was prepared by boiling $[NH_4][VO_3]$ with 10% acetic acid, the compounds used were purchased from Koch–Light Ltd. and used without further purification. The finely powdered samples were pressed with terephthalic acid to form discs (40 mm diameter) which could be inserted into the spectrometer.

*X*-Ray emission spectra were obtained using a Philips PW 1410 XRF spectrometer equipped with a tungsten-anode *X*-ray tube operated at 40 mA (60 kV). The spectrometer was evacuated to *ca.* $10^{-3}$ Torr. In order to obtain good resolution of the characteristic *X*-rays emitted by a sample it is necessary to work at a high angle of incidence ($\theta$) to the diffracting crystal [the differential of Bragg's law is $(d\theta/dE) = -E^{-1}\tan\theta$, where $E$ is the *X*-ray energy]. In the experiments reported here fourth-order diffraction from an ammonium dihydrogenphosphate (ADP 101, $2d$ = 1 062.8 pm) crystal was used which gave values of $\theta$ in the range 57—60° for vanadium $K_\beta$ *X*-rays. The *X*-rays were detected using a proportional counter (1 μm Mylar window), and amplified and counted using Harwell 2000 series electronics. In all cases the spectra were obtained as a ratemeter output on a chart-recorder trace. The slowest possible scanning speed (0.25° $\min^{-1}$) was used in order to obtain the best counting statistics. The peak width at half height which can be achieved with this type of spectrometer operated as described above is limited by the quality of the diffracting crystal and by the degree of collimation brought about by the Soller slits. In this work fine collimation was used, *i.e.* 150 μm spacing between the blades of a collimator giving an angular divergence of *ca.* ±0.1°. This gave a peak width at half height, for monochromatic radiation of 5 450 eV and with a perfect diffracting crystal, of *ca.* 6.5 eV, which limits the resolution that can be obtained.

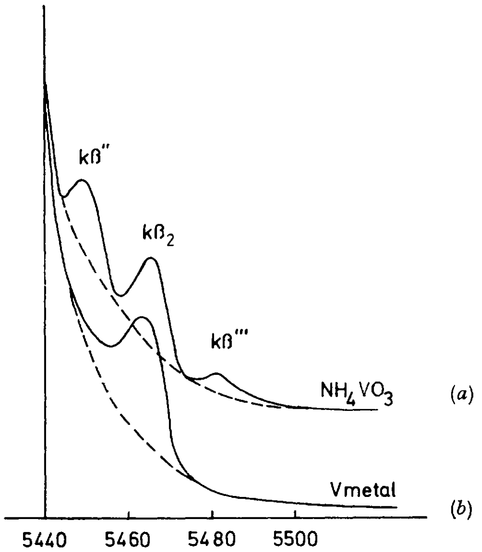

**FIGURE 1** Typical spectra from the $K_{\beta_2}$ region: (*a*), $[NH_4][VO_3]$; (*b*), V (metal); (— — — —), estimated background

## RESULTS

The peaks $K_{\beta_{2,5}}$ and $K_{\beta''}$, *etc.*, were found on the high-energy side of the intense $K_{\beta_{1,3}}$ peak. A typical experimental result is shown in Figure 1; a smooth curve has been drawn through the noise on the ratemeter trace. $K_{\beta_{2,5}}$ And related peaks were unfortunately not completely resolved from $K_{\beta_{1,3}}$. It was therefore necessary to estimate the 'tail' of the intense peak as a curve. This was done for all the spectra of the compounds discussed in this paper, and the results are shown in Figure 2. Because of the uncertainties inherent in such a procedure, the relative intensities of the peaks in these spectra could not be measured with great accuracy but even so the general features could be observed without doubt. These are the main $K_{\beta_{2,5}}$ peak, and for most compounds low-energy $K_{\beta''}$ and high-energy $K_{\beta'''}$ satellites. The origins of these peaks and of the shifts in their energies brought about by changes in the ligands are discussed in detail below. The energies of these peaks and also of $K_{\beta_{1,3}}$ and $K_{\alpha 1,2}$ are summarised in Table 1.

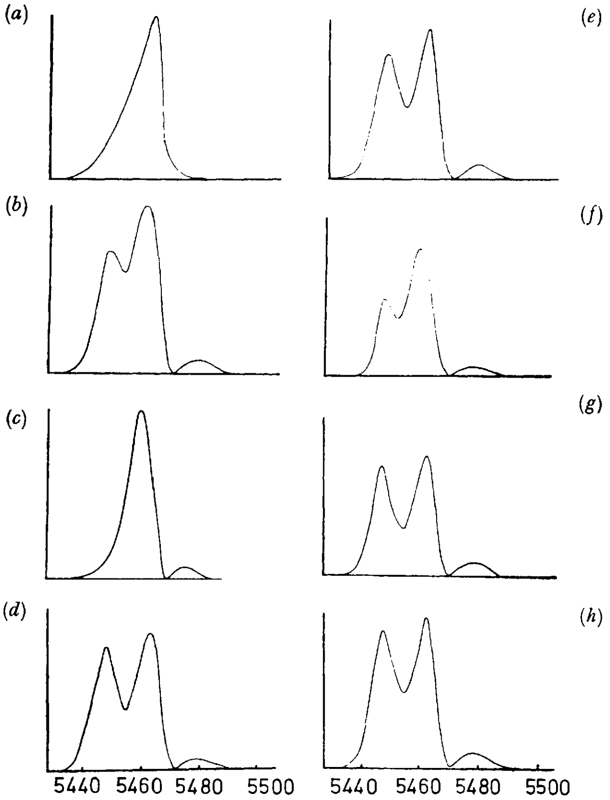

**FIGURE 2** $K_{\beta_2}$ Spectra of (*a*) V (metal), (*b*) $[V(pd)_3]$, (*c*) $VF_3$, (*d*) $V_2O_5$, (*e*) $VO_2$, (*f*) $[VO][SO_4]$, (*g*) $[NH_4][VO_3]$, and (*h*) $[NH_4][V_3O_8]$. The high-energy tail of $K_{\beta_{1,3}}$ has been substracted

## DISCUSSION

With the exception of vanadium metal, the trifluoride, and ammonium trioxovanadate, the vanadium atom in all the compounds studied here is surrounded by six oxygen atoms. In some cases, *e.g.* vanadium(III) pentane-2,4-dionate,[15] the arrangement probably approximates to a regular octahedron, in others, *e.g.* vanadium pentaoxide,[16] the arrangement is highly irregular. Despite these differences it is convenient to discuss the spectra of this group of compounds together to see if effects due to formal valence or distortion of the ligand environment can be discerned and distinguished.

In all these examples the general appearance of the spectra is similar. The most intense peak ($K_{\beta_{2,5}}$) is at *ca.* 5 460 eV. There is a lower-energy satellite peak ($K_{\beta''}$) which is almost as intense as $K_{\beta_2}$ at *ca.* 5 448 eV and a weak high-energy satellite at 5 479 eV ($K_{\beta'''}$). Since the vanadium 1*s* ionisation energy is 5 465 eV,[17] $K_{\beta'''}$ cannot result from a normal transition from an occupied bound m.o. to a 1*s* vacancy, its origin is discussed in a later section. On the other hand, there seems no reason why the two peaks $K_{\beta_{2,5}}$ and $K_{\beta''}$ should not have a conventional origin; electronic transitions from m.o.s with 4*p* character to a vacancy in a 1*s* orbital. The existence of two peaks at *ca.* 12—15 eV apart from compounds where oxygen is a ligand is very similar to that observed when main-group elements are bonded to oxygen.[2]

TABLE 1

Energies and relative intensities of vanadium *X*-ray emission peaks

| | Relative intensities [a] | | | | | | |
|---|---|---|---|---|---|---|---|
| | $K_{\beta_{2,5}} : K_{\beta_{1,3}}$ | $K_{\beta''} : K_{\beta_{2,5}}$ | $K_{\alpha_{1,2}}$ | $K_{\beta_{1,3}}$ | $K_{\beta''}$ | $K_{\beta_{2,5}}$ | $K_{\beta'''}$ |
| V (metal) | 0.03 : 1 | | 4 952.2 | 5 427.3 | | 5 462.9 | |
| $[V(pd)_3]$ [b] | 0.01 : 1 | 0.72 : 1 | 4 951.9 | 5 426.9 | 5 449.0 | 5 460.5 | 5 478.1 |
| $VF_3$ | 0.025 : 1 | *c* | 4 952.0 | 5 426.9 | *c* | 5 459.9 | 5 476.3 |
| $[VO][SO_4]\cdot 5OH_2$ | 0.016 : 1 | 0.60 : 1 | 4 951.8 | 5 426.6 | 5 448.4 | 5 460.5 | 5 478.7 |
| $VO_2$ | 0.032 : 1 | 0.82 : 1 | 4 951.9 | 5 426.9 | 5 448.1 | 5 462.0 | 5 478.1 |
| $V_2O_5$ | 0.04 : 1 | 0.89 : 1 | 4 951.8 | 5 426.3 | 5 448.1 | 5 462.9 | 5 478.7 |
| $[NH_4][VO_3]$ | 0.038 : 1 | 0.90 : 1 | 4 951.8 | 5 426.6 | 5 448.1 | 5 462.9 | 5 478.7 |
| $[NH_4][V_3O_8]$ | 0.038 : 1 | 0.92 : 1 | 4 951.8 | 5 426.3 | 5 448.1 | 5 463.2 | 5 478.7 |

[a] Estimated from peak heights. [b] pd = Pentane-2,4-dionate. [c] Not observed (see text).

TABLE 2

| Relative intensities of *X*-ray emission | $[VO_4]^{3-}$ | | | $[CrO_4]^{2-}$ | | | $[MnO_4]^-$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_{\beta_{1,3}}$ | : $K_{\beta''}$ : | $K_{\beta_{2,5}}$ | $K_{\beta_{1,3}}$ : | $K_{\beta''}$ : | $K_{\beta_{2,5}}$ | $K_{\beta_{1,3}}$ : | $K_{\beta''}$ : | $K_{\beta_{3,5}}$ |
| Expt., ref. 6 | 1 | 0.0022 | 0.019 | 1 | 0.0024 | 0.0026 | 1 | 0.017 | 0.019 |
| Expt. | 1 [a] | 0.0034 [a] | 0.0038 [a] | | 0.60 [b] | 1 | | | |
| *Ab initio* calc., ref. 8 | | 27 | 3 + 66 | | 61 | 3 + 91 | | 69 | 6 + 86 |
| % Central-metal atomic orbital in various m.o.s [c] | | | | | | | | | |
| | $3t_2$ | $4t_2$ | $5t_2 + 6t_2$ | $3t_2$ | $4t_2$ | $5t_2 + 6t_2$ | $3t_2$ | $4t_2$ | $5t_2 + 6t_2$ |
| Ref. 8 3*p* | 96.7 | 0.6 | 0 + 0.5 | 95.7 | 1.2 | 0 + 0.8 | 95.9 | 1.0 | 0 + 0.6 |
| Ref. 8 4*p* | 0.3 | 4.9 | 4.1 + 10.6 | 0.3 | 3.6 | 4.7 + 5.1 | 0.2 | 2.5 | 2.7 + 3.2 |
| Ref. 9, $[CrO_4]^{2-}$<br>Ref. 10, $[MnO_4]^-$ | | | | | 17.1 | 3.3 + 7.5 | | 8 | 3 + 4 |

[a] This work. [b] Ref. 18. [c] The numbering of m.o.s is taken from ref. 8; data from other sources have been altered where necessary.

*Vanadate and Related Anions.*—The vanadate ion has attracted the attention of other workers, usually in comparison with the isoelectronic chromate and permanganate ions, and attempts have been made to identify the origins of the $K_{\beta_{2,5}}$ and $K_{\beta''}$ peaks. Relative intensities as recorded by Best [6] (whose resolution was better than that reported in this paper) and as calculated by Connor *et al.*[8] using *ab initio* methods are given in Table 2 together with the atomic composition of relevant orbitals by Clack (CNDO) [9] and Prins (INDO).[10]

It can be seen that the *ab initio* calculations give a rather poor estimate of the $K_{\beta_{2,5}} : K_{\beta''}$ intensity ratio for vanadate but that agreement improves through chromate to permanganate. It is unfortunate that the calculations of Connor do not describe the particular atomic orbitals which contribute to the computed *X*-ray intensities, neither do they estimate the relative intensity of the $K_{\beta_{1,3}}$ peak. This would have permitted the contribution made by 3*p* orbitals to the intensities of *X*-ray emissions from valence-shell orbitals to be assessed. The importance of 3*p* character was proposed by Best, whose enigmatic calculations attempted to estimate the $K_{\beta_{1,3}} : K_{\beta''}$ intensity ratio for chromate. The result, 0.07 : 1, can be compared with 0.02 : 1 experimentally observed (Table 2); this agreement was said to be 'acceptable.' In these calculations **4*p*** orbitals were ignored since it was felt that the Cr 4*p*–O 2*s* ionisation-energy difference (i.e.d.) would be too large for effective overlap and that the integral $\int \psi_{1s} P \psi_{4p}\, d\tau$ would be too small. However, the Cr 4*p*–O 2*s* i.e.d. of 20 eV is very similar to that of Cr 3*p*–O 2*s* (18.3 eV) and estimates of the transition integral involving 4*p* orbitals suggest that it is between 10 and 15% of the corresponding integral with **3*p*** orbitals. These estimates are taken from heavier elements where $K_{\beta_2}$ and $K_{\beta_{1,3}}$ can be compared directly. It therefore seems unreasonable to exclude 4*p* orbitals as proposed by Best; they are included in the other calculations discussed in this paper.

In the orbital approximation the relative intensities

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[15] B. Morosin and H. Montgomery, *Acta Cryst.*, 1969, **B25**, 1354.

[16] A. Byström, K-A. Wilhelmi, and O. Brotzen, *Acta Chem. Scand.*, 1950, **4**, 1119.

[17] J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.*, 1967, **39**, **125**.

[18] A. T. Shoovaev and G. M. Koolyani, *Izvest. Akad. Nauk, U.S.S.R.* (*Ser. Fiz*), 1963, **27**, 322.

of $X$-ray emission peaks should be directly related to the relative amounts of atomic orbitals present in the various m.o.s.[2] Thus that part of the $K_{\beta_{2,5}}$ and $K_{\beta''}$ peaks which is to be ascribed to $3p$ character in these orbitals can be directly estimated from Table 1. In all cases it is between 0.5 and 1.2% relative to $K_{\beta_{1,3}}$, *i.e.* appreciable but insufficient to explain completely the observed relative intensities of these peaks. Perhaps of greater importance than a correct intensity estimate is the fact that for chromate and permanganate the observed $K_{\beta''} : K_{\beta_{2,5}}$ ratio is the reverse of that which would be predicted from $3p$ character alone. If it is assumed that $\int\psi_{1s}P\psi_{4p}\,d\tau$ is *ca.* 10% of $\int\psi_{1s}P\psi_{3p}\,d\tau$ as suggested above, it is possible to estimate the '$4p$' contribution to the relative intensity of the $K_{\beta_{2,5}}$ and $K_{\beta''}$ peaks. For vanadate the $3p$ and $4p$ contributions are comparable for $K_{\beta''}$ and 1 : 3 for $K_{\beta_{2,5}}$. The intensity, relative to $K_{\beta_{1,3}}$, of the latter peak is well estimated but low (1.1 instead of 2.2%) for $K_{\beta''}$. The experimental data presented here would seem to be in somewhat better agreement with calculations than that of Best. Fair agreement is also found for chromate and permanganate. It is interesting to note that Clack's CNDO results for chromate predict (Cr $3p$ was ignored as suggested by Carlson[19]) $4p$ contributions to $4t_2$ and $5t_2 + 6t_2$ orbitals opposite to those calculated by the *ab initio* method, and which would, if $4p$ orbitals alone determined $K_{\beta_{2,5}}$ and $K_{\beta''}$ intensities, also predict the wrong ratio for these peaks (*i.e.* $K_{\beta''} > K_{\beta_{2,5}}$). The INDO calculations and the *ab initio* calculations for permanganate both seem in fair agreement with each other and with the experimental result of $K_{\beta_{2,5}}$ and $K_{\beta''}$ peaks of comparable intensity, with the former a little more intense than the latter.

It therefore seems reasonable to conclude that both *ab initio* and INDO calculations are capable of calculating fairly accurately relative $X$-ray emission intensities. Further, it has been shown that the $K$ emission features associated with valence-band orbitals derive their intensity not only from $4p$ character but also from the participation of $3p$ orbitals. As would intuitively be expected, $3p$ character is greater in the more tightly bound $4t_2$ orbitals than in $5t_2$ or $6t_2$ orbitals. This provides a simple explanation for the most remarkable feature of these transition-metal spectra (Figure 2) when they are compared with main-group compounds (*e.g.* silicate or sulphate), *i.e.* the very high relative intensity of the lower-energy satellite peak $K_{\beta''}$ to the main valence-band peak $K_{\beta_{2,5}}$ (comparable peaks in second-row main-group compounds[2] are $K_{\beta''}$ and $K_{\beta_{1,3}}$ with a typical intensity ratio of 1 : 5).

*Vanadium Oxidation States.*—Small changes in $K_\beta$ emission energies are observed (Table 1) when the oxidation state of vanadium is altered even when the first co-ordination sphere remains wholly composed of oxygen atoms. But because the resolution between the $K_{\beta''}$ and $K_{\beta_{2,5}}$ peaks is poor it is not possible to determine very accurately either the energies or the relative intensities of these peaks. Even so qualitative trends, as a function of the valency of the vanadium, can be discerned. The overall shift in the $K_{\beta_{2,5}}$ peak of 2.5 eV in going from $V^{III}$ to $V^{V}$ is probably greater than can be explained by the deficiencies of resolution; the corresponding shift of $K_{\beta''}$ is more difficult to determine. Estimates of relative intensities are particularly difficult because of the underlying 'tail' from $K_{\beta_{1,3}}$ (Figure 1) and the figures given in Table 1 are probably subject to an error of at least ±20%. Despite these difficulties it does seem reasonable that on increasing the formal oxidation state of vanadium from III to V in an octahedral environment of oxygen atoms: (*i*) $K_{\beta_{2,5}}$ shifts to higher energies by *ca.* 2.5 eV; (*ii*) $K_{\beta_{2,5}} : K_{\beta_{1,3}}$ relative intensity increases by a factor of *ca.* 2; and (*iii*) $K_{\beta''} : K_{\beta_{2,5}}$ relative intensity increases from *ca.* 2 : 3 to *ca.* 1 : 1. {It is interesting to note that comparable effects [(*i*) and (*iii*)] are observed[18] for $Cr_2O_3$ and $[CrO_4]^{2-}$, $K_{\beta_{2,5}}$ shifts to higher energies by *ca.* 4 eV and $K_{\beta''} : K_{\beta_{2,5}}$ increases from *ca.* 0.25 : 1 to *ca.* 0.6 : 1.}

In the absence of more sophisticated calculations these trends can be rationalised by means of simple m.o. theory.[2] In an octahedral ($O_h$) arrangement of ligand atoms the valence-shell orbitals of vanadium will belong to the irreducible representations $3d$ ($e_g$ and $t_{2g}$), $4s$ ($a_{1g}$), and $4p$ ($t_{1u}$). Ligand orbitals orientated along the V–O bonds will transform as $a_{1g} + t_{1u} + e_g$. Only $K$ emission spectra are discussed in this paper and so only the $t_{1u}$ orbitals need be considered in detail. When the formal oxidation state of vanadium is increased the ionisation energies in all the atomic orbitals will be increased. Assuming the vanadium $4p$ ionisation energy to be less than that of oxygen $2p$, the interactions between oxygen $2s$ and $2p$ orbitals and the vanadium $4p$ orbitals can be treated in an analogous manner to those between main-group atom $p$ and ligand $s$ and $p$ orbitals. Moving to the right in the Periodic Table has the same effect as increasing the formal valence; valence-shell $p$ orbitals become more tightly bound. Thus it is to be expected that an increase in the formal oxidation state of vanadium will result in an increase in the (small) amount of $4p$ character in $t_{1u}$ ($\sigma$) m.o.s that are mostly $2p$ ligand in nature. This provides an explanation for the increase in relative intensity of the $K_{\beta_{2,5}}$ peak [(*ii*) above]; the intensity of the $K_{\beta_{1,3}}$ peak can be used as a reference since the $3p$ electron population will not be affected by chemical changes. Although the amount of $4p$ character will increase in these m.o.s, their ionisation energy will be largely determined by the excess of $2p$ ligand character. This ionisation energy is rather indifferent to changes in the central-atom $p$-orbital ionisation energy, at least over a limited range.[2] Thus on oxidation it is to be expected that the valence $t_{1u}$ (V $4p$–O $2p$ $\sigma$) orbitals will have an almost unchanged ionisation energy whilst that of the vanadium $1s$ orbital will increase. In this way the observed increase in $K_{\beta_{2,5}}$ emission energy with oxidation of the vanadium may be understood [(*i*) above]. M.o. calculations were also made[2] to determine the way in which central-atom $p$ character entered

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[19] K. D. Carlson and C. Moser, *J. Chem. Phys.*, 1966, **44**, 3259.

orbitals that were mostly ligand 2*p* and 2*s* as a function of *p* ionisation energy. As might be expected, the *p* contribution to the '2*s*' orbitals increased relative to the contribution to '2*p*' orbitals thus providing a rationalisation of (*iii*), the increase in the $K_{\beta''} : K_{\beta_{2,5}}$ intensity ratio energy from $V^{III}$ to $V^{V}$.

*Ammonium Trioxovanadate,* $[NH_4][VO_3]$.—The features of the *X*-ray emission spectra of this compound are very similar to those of ammonium trivanadate, $[NH_4][V_3O_8]$. The bonding commitments of V 4*p* orbitals in four- and six-co-ordinate situations must therefore be quite similar. Certainly there would not seem to be any aspects of these spectra that would enable the different co-ordination numbers to be distinguished.

*Vanadium Trifluoride.*—The vanadium atom is here octahedrally co-ordinated but by fluorine and not by oxygen atoms. The most dramatic effect is the disappearance of the $K_{\beta''}$ peak from the spectrum. By analogy with second-row main-group elements, the $K_{\beta''}$ peak associated with fluorine ligands is anticipated to have an energy *ca.* 20 eV less than $K_{\beta_2}$.[2,20] Unfortunately at this energy (5 440 eV) $K_{\beta_{1,3}}$ has considerable intensity which is rapidly increasing with decreasing energy. Any satellite peak which might be present cannot, therefore, be observed. The actual energy of $K_{\beta_{2,5}}$ is of interest since it is the lowest observed in this suite of compounds. Since fluorine 2*p* orbitals are more tightly bound that their oxygen counterparts, this is perhaps not unexpected. However, fluorine is more electronegative than oxygen and so V 1*s* might well be more tightly bound in vanadium trifluoride than in other $V^{III}$ compounds [*e.g.* vanadium(III) pentane-2,4-dionate]. This would counteract the tendency for $K_{\beta_{2,5}}$ to have a much lower energy in fluoro- than in oxo-ligand compounds. This effect has been quantitatively studied for silica and the hexafluorosilicate anion.[21] The increase in the Si 1*s* ionisation energy, estimated from Si-$K_{\beta}$ *X*-ray fluorescence and Si 2*p* *X*-ray photoelectron experiments, was almost exactly equal to the increase in binding energy of the valence-shell orbitals so that Si-$K_{\beta_{1,3}}$ is almost identical for the two compounds. It therefore seems reasonable to propose a similar explanation for the very slight increase in the $K_{\beta_{2,5}}$ energy in going from the pentane-2,4-dionate to the fluoride.

*The* $K_{\beta'''}$ *Peak.*—This peak has a higher energy than can be accounted for by a conventional transition from an occupied orbital to an inner vacancy. Two general mechanisms suggest themselves: one that this is a transition in a doubly ionised atom; and the other that it represents the relaxation of an electronically excited atom (atom here is used to describe vanadium in its original chemical state).

Interesting features of $K_{\beta'''}$ are that it is only present as a clearly defined peak in chemical compounds and that the $K_{\beta_2}$–$K_{\beta'''}$ energy difference is remarkably constant at *ca.* 15 eV. If this peak is due to transitions in a doubly ionised atom, there would seem to be no good reason why it should not also be observed for metallic vanadium. A feature of the peak shapes of *X*-ray emission spectra, however, is that they are broad and distorted for metals but quite sharp and symmetrical for compounds.[1] Peak shape reflects the band structure of the solid and absorption spectra should show the same distinction, because the nature of the underlying orbital structure is similar for occupied and unoccupied m.o.s. A weak diffuse peak from an electronically excited atom in the metal might not be detected but a narrower sharp peak from a compound would be. It therefore seems possible that the $K_{\beta'''}$ feature is due to relaxation of a vanadium atom in which an electron has not been ejected by the incident *X*-radiation but rather excited to a specific antibonding m.o. which would be in the continuum. It is hoped to investigate the absorption spectra of these compounds to provide corroboration for this idea. (Similar mechanisms have recently been proposed to explain high-energy emission features in both sulphur hexafluoride [22] and nitrogen.[23])

*Conclusions.*—An analysis of m.o. calculations, in the light of vanadium *K* emission spectra, shows that 3*p* and 4*p* character in valence-shell m.o.s must be considered for a satisfactory explanation of the relative intensities of the $K_{\beta''}$ and $K_{\beta_{2,5}}$ peaks. However, for a qualitative rationalisation of changes in the $K_{\beta_{1,3}} : K_{\beta''} : K_{\beta_{2,5}}$ relative intensities and of changes in the $K_{\beta_{2,5}}$ emission energy with the formal oxidation state of vanadium it is sufficient to consider only the variations in 4*p* character as described by simple m.o. theory. The participation of 4*p* orbitals increases from $V^{III}$ to $V^{V}$, *i.e.* the bonds become more covalent as might be expected. The contribution made by 3*d* character in valence-shell m.o.s to the intensities of *K* emission peaks seems to be negligible: it is therefore better to refer to them as $K_{\beta_2}$ than $K_{\beta_{2,5}}$ or $K_{\beta_5}$.

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