CHAPTER 4

VANADIUM K-ABSORPTION EDGE STRUCTURE
4.1. INTRODUCTION

X-ray absorption spectrum has traditionally been divided into a low energy region the so-called X-ray absorption near edge structure (XANES), in which the transitions are to bound states\textsuperscript{1-3}, and a high energy region, the so-called extended X-ray absorption fine structure (EXAFS), where the transitions are to free electron states\textsuperscript{4-5}. Recently, as mentioned in Chapter 1, high intensity X-ray sources have become available whose intensities are about $10^5$ times higher than those previously available. This results in improved signal to noise ratios, which allow meaningful measurements to be made even on dilute systems\textsuperscript{5-6}.

In this Chapter we present our measurements, made with X-rays from Rigaku X-ray generator, on K X-ray absorption spectra of superconducting oxides containing vanadium and several model vanadium compounds. The model compounds which we have studied in the present work are CrVO\textsubscript{4}, GdVO\textsubscript{4}, BiVO\textsubscript{4}, Cd\textsubscript{4}V\textsubscript{2}O\textsubscript{7}, Ca\textsubscript{3}Fe\textsubscript{3}GeVO\textsubscript{12}, Pb\textsubscript{5}(VO\textsubscript{4})\textsubscript{3}Cl, Zn\textsubscript{2}(VO\textsubscript{4})\textsubscript{3}, NaVO\textsubscript{3}, VO(acac)\textsubscript{2}, VO(bzac)\textsubscript{2}, (NH\textsubscript{4})\textsubscript{4}[VO-dd-tart]\textsubscript{2}.2H\textsubscript{2}O, VOPC, VOTPP, VOMoO\textsubscript{4}, V\textsubscript{2}O\textsubscript{5}, VO, (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}.VSO\textsubscript{4}.6H\textsubscript{2}O, V\textsubscript{2}O\textsubscript{3}, SmVO\textsubscript{3}, V\textsubscript{2}S\textsubscript{3}, VN, VO\textsubscript{2}, V\textsubscript{4}O\textsubscript{7}, VC, [VO(hshed)(acac)], PbV\textsubscript{2}O\textsubscript{6} and Ca\textsubscript{3}V\textsubscript{10}O\textsubscript{28}.16H\textsubscript{2}O. The superconducting oxides of vanadium include compounds of composition Tl\textsubscript{1-x}V\textsubscript{x}Sr\textsubscript{2}(Ca\textsubscript{0.8}V\textsubscript{0.2})Cu\textsubscript{2}O\textsubscript{y}, where x = 0.2, 0.3, 0.4 and 0.5. Electronic transitions from the 1s to 3d, 4s and 4p states, in the model compounds as well as in superconducting oxides have been assigned to different spectral features observed in the vanadium K-edge spectra on the basis of atomic model of Shulman et al\textsuperscript{7} and others\textsuperscript{8-11}.

\begin{align*}
\text{tart} & = \text{tartrate} (C_4H_2O_6) \\
\text{acac} & = \text{acetylacetonate} (C_5H_7O_2) \\
\text{bzac} & = \text{benzoylacetonate} (C_{10}H_9O_2)
\end{align*}

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4.2. RESULTS AND DISCUSSION

The zero of the energy scale of the XANES spectra was taken with respect to the first inflection point of the vanadium metal in the first derivative spectrum at 5465.0 eV, which, according to Bearden and Burr, marks the threshold or onset of photoejection of the 1s electron in vanadium metal. All the spectra were normalized by fitting a linear function to the pre-edge data and fitting cubic spline to the EXAFS region of the data up to 400 eV, extrapolating both functions to the zero of energy i.e. the inflection point energy [and taking the difference (the edge step height)], subtracting the pre-edge data function from each point in the experimental spectrum, and dividing by the step height. This procedure results in a normalization of the data to the unit step height. The energy positions of the important spectral features in all the compounds studied in this work are given in Table 4.1.

4.3. ASSIGNMENT OF ELECTRONIC TRANSITIONS

Before discussing our results on X-ray absorption measurements, it would be interesting to mention here that in the case of X-ray absorption spectra of transition metal compounds studied by various authors, the K-absorption edges exhibit a weak low-energy peak at the threshold followed by a shoulder on a rising absorption curve that culminates in a strong peak. Through an examination of a series of cubic perovskites of first-row transition metals, KM₃ (where M = Mn, Fe, Co, Ni, and Zn), Shulman et al. assigned the lowest energy features in such edges.
as 1s → 3d transitions, the intermediate feature as a 1s → 4s transition, and the dominant peak as 1s → 4p transition. It is observed by these authors that the experimentally measured energies of these features agree rather well with the spectroscopic energy levels of the Z+1 (where Z is an atomic number) ions. Similar assignments have been made previously by other authors\textsuperscript{8-11}.

The assignments, 1s → 3d, 1s → 4s and 1s → 4p, although useful in a qualitative sense, are unsatisfactory in one respect. They are based on an atomic model for the available orbitals that does not allow for covalent bonding. Clearly, the final orbitals for the lower energy transitions cannot be of pure d or s character, since the angular momentum selection rules forbid 1s → n d or 1s → (n+1) s transitions. Shulman et al\textsuperscript{7} have claimed that vibronic mixing of s, p and d characters makes the low energy transitions allowed. However, in many complexes covalent interactions between metal and ligands could also cause such mixing, in which case a molecular orbital (MO) description of the electronic transitions would be more desirable. In section 4.4, the MO scheme has therefore been used for interpretation of X-ray absorption spectra.

Most of the studies on the near-edge structure so far carried out by various authors have been primarily experimental in nature. Comparisons were made only with calculated molecular energy level spacings; no transition strengths were included. However, more quantitative calculations for the near-edge structure in transition-metal compounds have been done and few results have been published. Bair and Goddard\textsuperscript{22} have carried out \textit{ab initio} self-consistent field calculations on the excited states of the CuCl\textsubscript{2} molecule involving excitations of the Cu 1s orbital into bound valence and unbound virtual orbitals. These authors have calculated both the absolute excitation energies and the transition strengths, and considered the presence of a fully
relaxed core hole, in their theoretical method based on a multielectron model utilizing a Hartree-Fock configuration-interaction approach. They have found that the weak pre-edge peak is indeed due to a transition to a partially unoccupied orbital of a primarily metal 3d character, in agreement with the above discussion. The main absorption peak at 8993 eV is assigned as a transition to the orbitals that are primarily of a metal 4p character (1s → 4p_z) again in agreement with some of the above studies. However, the shoulder (the lower energy feature at 8986 eV) is not assigned to any single-electron transition. The 1s → 4s monopole transition strength is found to be far too weak to be observed and appears at the wrong energy to fit the shoulder peak data. Rather, this feature is reassigned by these authors to a "shake down" satellite transition involving a Cu 1s → 4p_z transition simultaneous with ligand-to-metal charge transfer.

A similar interpretation has recently been proposed²³-²⁴ for the polarised spectra of CuCl_2·2H_2O and (creat)_2CuCl_2. Satellite peaks, which are pronounced in inner-shell XPS studies of many transition-metal complexes²⁵-²⁹, are predicted to be significantly reduced in intensity in X-ray absorption edge studies due to the shielding of the valence electrons when the photoelectron is in the low-energy threshold region. A previous study³⁰ comparing the XPS and X-ray absorption spectra of FeCl_2, MnCl_2 and CoCl_2 found low intensity satellites to the high energy side of the principal absorption maxima at energies corresponding to those expected on the basis of the prominent satellite splittings found in XPS. More rigorous calculations have been reported by Kutzler et al³¹ who have performed self-consistent field Xα multiple scattering wave calculations for the near-edge of iron, chromium and molybdenum compounds. Like Bair and Goddard, they calculated one-electron transition strengths into bound and continuum states including the fully relaxed core hole. The results of these numerical studies indicate that a molecular
cage defined by the first shell of ligands, which breaks the inversion symmetry at the metal atom site, can make transition from a 1s electron state to a bound state of a mainly nd character possible via admixture with p orbitals from liganding atoms. They also show that the shoulder or kink, which has been assigned by several authors to a $1s \rightarrow (n+1)s$ transition, appears to be an inherent feature of the continuum and that the principal absorption maximum correspond to a $1s \rightarrow (n+1)p$ transition. However, it is worth noting that the results of Kutzler et al fail to predict the various shoulder peak splittings observed in the measured spectra of transition-metal compounds. These authors speculated that many-electron processes (such as shake-down transition considered by Bair and Goddard) may be involved but they do not attempt to incorporate such effects into their calculations.

From the above studies we see that interpretation and calculation of the near-edge structure for the transition-metal compounds is much less clear cut. Many-electron effects due to an incompletely screened core hole appear to be sufficiently important to alter the simple molecular orbital or symmetry-based transition scheme invoked by various investigators. Although it appears that we are safe in labelling the pre-edge peak and main absorption maximum as $1s \rightarrow 3d$ and $1s \rightarrow 4p$ transitions, respectively, more corroborating calculations are needed before a definite assignment of the shoulder peak is possible.

Vanadium K-absorption spectra in vanadium metal and typical vanadium compounds are shown in Figures 4. 1, 2, 3, 4 and 5. In Figure 4.6 are given the near-edge absorption spectra of vanadium in superconductors of the composition $Tl_{1-x}V_xSr_2(Ca_{0.8}Y_{0.2})Cu_2O_y$, where $x = 0.2, 0.3, 0.4$ and 0.6. These spectral curves were obtained by averaging the results of a very large number of spectra recorded for each sample. For the superconductors, 25 scans of each were recorded in order to confirm all the fine
Figure 4.1: X-ray absorption spectrum of Vanadium metal
Figure 4.2: X-ray absorption spectra of VO, V\textsubscript{2}O\textsubscript{3}, V\textsubscript{4}O\textsubscript{7}, V\textsubscript{2}O\textsubscript{4}, V\textsubscript{2}O\textsubscript{5} and NaVO\textsubscript{3}
Figure 4.3: X-ray absorption spectra of CrVO₄, GdVO₄, Zn₃(VO₄)₂, Ca₃Fe₃VGeO₁₂ and Pb₅(VO₄)₃Cl
Figure 4.4: X-ray absorption spectra of VOPc, VOTPP, \((\text{NH}_4)_4[\text{VO tart}]\cdot 2\text{H}_2\text{O}\), VO(bzac)_2 and VO(acac)_2
Figure 4.5: X-ray absorption spectra of Tutton's salt, PbV$_2$O$_6$, Ca$_3$V$_{10}$O$_{28}$.16H$_2$O, [VO(hshed)(acac)], SmVO$_3$, V$_2$S$_3$ and VN
Figure 4.6: X-ray absorption spectra of $\text{Tl}_{1-x}\text{V}_x\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$, where $x = 0.2, 0.3, 0.4$ and 0.5
structure peaks.

It is observed from Figure 4.1 that the K absorption edge of vanadium metal splits into three components. In the case of the vanadium compounds the absorption discontinuity is seen to split into three or more components. Our results in this respect are in good agreement with those obtained by Wong et al.\textsuperscript{36} for vanadium metal and some of the compounds studied. For compounds viz. Zn\textsubscript{2}V\textsubscript{2}O\textsubscript{7}, PbV\textsubscript{2}O\textsubscript{6}, (NH\textsubscript{4})[VO-dd-tart]\textsubscript{2} \cdot 2H\textsubscript{2}O, Ca\textsubscript{3}Fe\textsubscript{3}GeVO\textsubscript{12}, GdVO\textsubscript{4}, etc., no experimental data are available for comparison.

We shall first discuss our results on the near edge structure in model compounds having vanadium ions at tetrahedral, square pyramidal and octahedral sites and then we shall use these results to extract structural information in the superconducting oxides of vanadium. The relevant structural data on all the compounds are presented in Table 4.2 (Refs. 37 - 61).

4.3.1. VANADIUM K - EDGE IN MODEL COMPOUNDS

The K-absorption near edge spectra of transition metal compounds are rich in information from which details on the coordination environment can be deduced. The profiles of the vanadium K - absorption edge in Figures 4.1, 2, 3, 4 and 5 show a pre-edge feature at the threshold followed by a shoulder on the rising absorption curve which culminates in a strong absorption peak. The pre-edge peaks are due to the transitions of the photoelectron to final states that are essentially vanadium 3d bound states. These transitions are quite sensitive to the crystal field\textsuperscript{62-63} due to ligands around vanadium and hence the number, position, and intensity of these pre-edge peaks give information about the coordination environment of vanadium.

The main reason for this can be found in the d\textsuperscript{0}, d\textsuperscript{1}, d\textsuperscript{2}, d\textsuperscript{3} electronic configurations of V\textsuperscript{5+}, V\textsuperscript{4+}, V\textsuperscript{3+} and V\textsuperscript{2+} ions respectively. All the d symmetry molecular levels are vacant.
completely or partially depending on the oxidation state of vanadium and available to receive the photoelectron to give \((1s)^1(3d)^1, (1s)^1(3d)^2, (1s)^1(3d)^3\) and \((1s)^1(3d)^4\) excited electronic configurations. The symmetry of the final state is that of the d levels since the 1s core hole is totally symmetrical and all other shells below the valence band are filled. Taking into account only the dipole electron transitions (\(\hat{0}_\text{dip}\) dipole operator), the transition moment is given by the general Fermi golden rule\(^6\)

\[
M \propto <\psi_{\text{ground}}|\hat{0}_\text{dip}|\psi_{\text{excited}}^2 [N(E)]
\]

\[
\delta(h\nu - E_{\text{ground}} + E_{\text{excited}})
\]

(4.1)

In this expression, \(N(E)\) is the number of vacancies in the excited states. This number is 0 or 1 or 2 in a molecular orbital description of a filled, singly occupied, or vacant orbital; \(\delta\) is a Dirac function, and the matrix element is a complex quantum function quite difficult to be computed exactly in the present state of the art\(^{22,31,65}\).

In a pure tetrahedral symmetry, the pre-edge absorption is an outstanding feature in the K-edge XANES spectra of vanadium compounds, as can be seen from Figure 4.3. In every spectrum, in Figure 4.3 an intense single peak is observed. It corresponds to a dipole-allowed transition from the 1s to admixed state formed from the 3d and 4p metal orbitals and from the 2p orbitals of neighbours.

In an octahedral symmetry, a weak pre-edge feature is observed (see Figure 4.2), the intensity of which is rather low due to the presence of an inversion centre at the V site \((\Gamma_0 = T_{1u})\). The weakness of the intensity is due to the absence of \(A_{1g}\) in the direct product and there is no more 3d-4p mixing. The presence of such weak transitions may be assigned\(^3\) to some
relaxation of the Laporte selection rules, by vibronic coupling, or to the interference of a quadrupolar mechanism, as already demonstrated in a square planar CuCl$_4^{2-}$ complex$^{66}$. 

The assignment of the first peak after threshold i.e. shoulder on the rising absorption curve (and other weak peaks between this shoulder and 1s $\rightarrow$ 3d peak) is still controversial$^{67-68}$. As mentioned earlier, according to the self-consistent $X_\alpha$ multiple scattering wave calculations of Kutzler et al$^{31}$, this feature, which has been assigned by several authors to a 1s $\rightarrow$ 4s transition, appears to be an inherent feature of the continuum, while, according to the \textit{ab initio} self-consistent field calculations of Bair and Goddard$^{22}$, this feature cannot be assigned to any single electron transition. Rather, this feature is reassigned by these authors as a 1s $\rightarrow$ 4p transition plus simultaneous shakedown. It appears always much below the main transition with weak intensity and it will not be discussed further. Nevertheless, its presence in the spectra of liquid samples studied by Sonaye$^{69}$ allows us to rule out any interpretation of this transition based only on 3d solid-state interactions. The remaining peak, i.e., the main absorption maximum can then be assigned to the transition of 1s electron to the 4p state. Since it is a dipole-allowed transition ($\Delta l = +1$), its intensity is expected to be more as compared to the intensities of the pre-edge and shoulder peaks.

As mentioned earlier, the profiles of the X-ray absorption spectra of tetrahedrally coordinated vanadium compounds given in Figure 4. 3 show a very intense pre-edge peak. The intensity of this pre-edge feature (in Figure 4. 4) is slightly lowered for compounds in which vanadium ion has square-pyramidal coordination and its intensity is the least for octahedrally coordinated vanadium compounds as can be seen from Figures 4. 2 and 4.
4.3.2. XANES SPECTRA AND SUPERCONDUCTING OXIDES

Since the discovery of superconductivity in the La-Ba-Cu-O and Y-Ba-Cu-O systems, there has been extensive research on the substitution of 3d transition metals. Unfortunately, the incorporation of transition elements into these superconducting oxides always has a detrimental effect on the transition temperature, $T_c$. Recently, Doi et al.\textsuperscript{71} have synthesized a monophasic TlSr$_2$CaCu$_2$O$_7$ compound. Which has single Tl-O sheets and tetragonal symmetry ($a = 3.7859$ Å and $c = 12.104$ Å: space group p4/mmm), but the material is not superconducting for the temperatures down to 4K. These authors proposed that the introduction of lead into TlSr$_2$CaCu$_2$O$_7$ would optimize the hole concentration and lead to superconducting at high temperatures. In fact, Subramanian et al.\textsuperscript{72} synthesized the compound (Tl$_{0.5}$Pb$_{0.5}$)Sr$_2$CaCu$_2$O$_7$ which is superconducting below 80K. In the case of the TlSr$_2$CaCu$_2$O$_7$ compound, the Cu valence is 2.5+, which appears to be too high and the compound is unstable and/or difficult to prepare as a single phase. Interestingly, a large number of 3d transition metal cations have accessible valencies of four and above. This aspect leads one to suggest that high valent 3d transition metals might play the same role as lead (4+) - if they substitute for Tl (3+) sites in TlSr$_2$CaCu$_2$O$_7$, rather than substituting in the Cu-0 framework. If this is possible, the substitution would reduce the overdoping of TlSr$_2$CaCu$_2$O$_7$ and give rise to a superconductor. This reasoning lead Liu et al.\textsuperscript{73-75} to synthesis of a new family of high-Tc superconductors in the system (Tl$_{1-x}$M$_x$)Sr$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{7-\delta}$ (M = Ti, Zr, Hf, V, Nb, and Ta). In this work, we have studied four superconducting oxides of the composition (Tl$_{1-x}$V$_x$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_{7-\delta}$, (x = 0.2, 0.3, 0.4 and 0.5) in order to study atomic environment of vanadium ions.

The vanadium K-edge spectra in superconducting oxides are shown in Figure 4.6. All the four oxides show a relatively
intense peak in the 1s → 3d region. The next peak (or a shoulder peak) in the spectra of these compounds appears ~10eV with respect to the inflection point on the absorption edge of vanadium metal. The main absorption peak corresponding to 1s → 4p transition in all the superconducting oxides lies in the energy region 16-18 eV. All the three pre-edge, shoulder and main absorption peaks are well within the range of quadruvalent or pentavalent compounds. There is no evidence of any transition in the spectra that would indicate the presence of V$^{3+}$ ions. In fact, TlSr$_2$CaCu$_2$O$_7$ type structure, if Tl$^{3+}$ ions are partially replaced by vanadium, one would expect the presence of V$^{3+}$ ions at Tl$^{3+}$ ion sites. Our results clearly indicate that the vanadium ions are present in quadruvalent or pentavalent state but in the trivalent state. Thus a comparison of the K-edge profiles in superconductors with the vanadium K-edges of model vanadium compounds gives indication of presence of V$^{4+}$ or V$^{5+}$ ions. This rules out the possibility of divalent or trivalent state of vanadium in the superconducting oxides. This is because all the divalent or trivalent compounds of vanadium show a very weak pre-edge peak and this is not observed in these compounds. The coordination number of vanadium ions from the comparison of their peaks with intense peak of reference compounds appear to be five.

4.4. MOLECULAR - ORBITAL APPROACH AND V K-EDGE STRUCTURE

It is well known$^{2-3}$ that the fine structure within about 20 to 25 eV of an absorption edge in a compound is characteristic of chemical bonding. Literature survey shows that the molecular orbital theory has been successfully employed by many workers to explain fine structure observed in the absorption edges of compounds. Fischer$^{34-35}$, Pendharkar and Mande$^{76}$, Obashi$^{77-78}$, Chetal and coworkers$^{79-81}$, Sarode and Pendharkar$^{82}$ have assigned the peaks of X-ray absorption near edge structure (XANES) to the
core electron transition to the vacant molecular orbital levels of appropriate symmetry formed from interaction of ligands with central metal atoms.

In the present work, a qualitative molecular orbital diagram for octahedral compounds like VO, V_2O_3 and V0_2, adapted from the book by Ballhausen and Gray is shown Figure 4.7. This diagram takes into account the interactions of the metal 3d, 4s and 4p orbitals and the 2s and 2p (σ, π) orbitals of the ligand. In this figure, solid, half open, and fully open circles represent electron pairs, unpaired electron and fully vacant states respectively. For octahedral group such as VO_6, which exist in a compound like VO, vanadium atom contributes five electrons (3d^3 4s^2) and six oxygen ligands contribute 36 electrons (2s^2 2p^4) to the formation molecular orbitals. However, the VO_6 ion has ten more electrons because of its negative charge. Therefore total number of electrons of VO_6 cluster contributed to the formation of the molecular orbitals is 51. After distributing all these electrons in the various molecular orbitals as shown in Figure 4.7, one finds that the orbitals below 2t^2g are completely filled. The antibonding orbital 2t^2g is partially vacant (half-filled) and the higher energy orbitals above 2t^2g are completely vacant. The partially vacant antibonding orbitals 2t^2g and completely vacant 3e_g have d symmetry and the empty antibonding orbital 3a_1g has s symmetry and the outermost empty antibonding 4t_1u level has p symmetry.

In VO, V_2O_3, V0_2 and other transition metal oxides, where transition metal ion is octahedrally coordinated to oxygen, the 3d band splitting is less than 2 eV. It is difficult to see two transitions from 1s core level to 3e_g and 2t^2g levels as the resolution of our spectrometer is ~ 4 eV. Therefore, the (3e_g, 2t^2g) levels. The shoulder and the main absorption maximum in Figure 4.2 can now be assigned to the transitions of the 1s electrons of the K shell to the vacant 3a_1g and 4t_1u molecular
Figure 4.7: Molecular orbital energy level scheme for octahedral vanadium compounds
orbital levels respectively.

It may be noted that the $1s \rightarrow (3e_g', 2t_{2g})$ and $1s \rightarrow 3a_{1g}$ transitions are dipole forbidden. However, as can be clearly seen from the molecular orbital diagram (Figure 4.7) some amount of the $p$ character from oxygen orbitals mixes up with metal orbital to form these molecular orbitals, making these two electronic transitions allowed. If the liganding atom is nitrogen or carbon or sulphur instead of oxygen, the same molecular orbital picture is valid. Furthermore, in some compounds vanadium has six ligands comprising nitrogen and oxygen atoms, the molecular orbital picture in this case will remain, to the first approximation, the same. Therefore, the absorption fine structure in such compounds can be interpreted in a similar way.

For vanadium compounds like GdVO$_4$, BiVO$_4$, wherein the vanadium ion is tetrahedrally bonded to the oxygen ligand, the molecular orbital picture is shown in Figure 4.8. It takes into account the interaction of metal 3d, 4s and 4p orbitals and 2s and 2p ($\sigma, \pi$) orbitals of oxygen ligands. The vanadium atom contributes 5 electrons and 4 oxygen atoms contribute 24 electrons to the formation of molecular orbitals. Taking into consideration the charge on the VO$_4$ cluster, the total number of electrons is 32. After distributing these electrons in various molecular orbitals of VO$_4$ ion as shown in Figure 4.8, one observes that the antibonding orbital 2e and the other antibonding orbitals viz. 4t$_2$, 3a$_1$ and 5t$_2$ are completely vacant. The 2e molecular level is formed from 3d metal orbitals and 2p orbitals of oxygen atom. The antibonding levels 4t$_2$ and 5t$_2$ have d+p admixture of metal character and s+p admixture of ligand. The 3a$_1$ level has the s character from metal and s+p character from ligand. Hence the electrons from the K level can go, in the X-ray absorption process, to all these levels without violating the dipole selection rules. Thus, like electron transitions in octahedral compounds, the pre-edge absorption peak can be
Vanadium Orbitals  Molecular Orbitals  Oxygen Orbitals

Figure 4.8: Molecular orbital energy level scheme for tetrahedral vanadium compounds

- $t_{2g}$
- $e_g$
- $t_{1u}$
- $e_u$

$A = \text{Crystal field splitting}$

$\bullet = \text{Electron pair} ; \ O = \text{Vacant state} ; \bigcirc = \text{Unpaired electron}$

$\Delta = \text{Crystal field splitting}$
attributed to the transition of 1s electron to the \((2e, 4t_2)\)
molecular orbitals, since the 3d level splitting is very small.
The shoulder peak and the main absorption maximum can be assigned
to the transition of the 1s electron to the \(3a_1\) and \(5t_2\) molecular
levels respectively. It may be interesting to note here that the
relative intensity of \(1s \rightarrow 3d\) transition in tetrahedrally
coordinated vanadium ions is relatively very large as compared to
that of vanadium compounds wherein vanadium ions are octahedrally
coordinated. The reason is obvious, if we compare the transitions
of 1s electron to \((2t_{2g}^\prime, 3e_g)\) and \((2e, 4t_2)\) levels in the
octahedral and tetrahedral compounds respectively. The level \(2t_{2g}^\prime\)
or \(3e_g\) has little \(p(\sigma,\pi)\) contribution from oxygen and hence the
intensity of \(1s \rightarrow (2t_{2g}^\prime, 3e_g)\) transition is very small in
octahedral compounds. However, the level \(4t_2\) (or \(2e\)) has a
relatively large amount of \(p\) contribution from metal and \(p(\sigma,\pi)\)
contribution from ligand. It means that the \(4t_2\) MO level has more
\(p\)-contribution and the pre-absorption peak corresponding to the
transition \(1s \rightarrow (2e, 4t_2)\) is more intense. This is the reason why
many workers\(^8,32,85-88\) have observed a very intense \(1s \rightarrow 3d\)
transition in vanadium, chromium and manganese compounds.

For square-pyramidally coordinated vanadium compounds viz.
\(\text{VO(bzac)}_2\), \(\text{V}_2\text{O}_5\) the qualitative molecular orbital diagram is not
available in literature. According to Figgis\(^87\), a probable
splitting pattern for the d-orbitals in a square-pyramidal
complex is similar to that in a square-planar complex. Wherein
the d level splits into four components. Similar thing is
expected in a square-pyramidal complex. A order of increasing
energy, the sequence of splitted orbitals given by Figgis\(^87\), is
\(b_2(d_{xy}), e(d_{xz}, d_{yz}), a_1(d_{z^2}), b_1(d_{x^2-y^2})\). All these antibonding
orbitals are empty if the vanadium ion is pentavalent. If it is
quadravalent, the \(b_2\) orbital will have one electron. The next
empty antibonding orbitals will be \(a_{1g}, a_{2u}\) and \(e_u\) which have
4s+2p_σ, 4p+2p_π and 4p+2p_σ characters respectively. As mentioned earlier, the d band splitting is very small, the pre-edge peak would be attributed to 1s electron transition to the empty molecular orbital (b_z, e, a_1, b_1). The shoulder of the K-edge and the principal absorption peak may be assigned to the transition of 1s electron to the vacant antibonding a_1g orbital and (a_2u, e_u) orbitals respectively. The relatively large intensity of the pre-edge peak is difficult to explain unless, a full description of MO diagram is available.

4.5. BOND LENGTH DETERMINATION FROM V K-EDGE STRUCTURE

As mentioned earlier, there is a growing interest in understanding the X-ray absorption near-edge structure (XANES) part of X-ray absorption spectra for local-structure determination in complex systems. According to Bianconi et al., XANES of transition metal compounds can be separated into two parts:

(a) the discrete part below the continuum edge, where the weak features are usually called pre-edge peaks (or prepeaks), due to transitions to unoccupied bound antibonding orbitals and

(b) the continuum part where the peaks are due to multiple-scattering resonances of the photoelectron, which are sensitive to both coordination geometry and interatomic distances.

The effect of the interatomic distance R has been shown to shift the multiple-scattering resonances in diatomic molecules, with a given geometry, following the rule K_R = const., where K_R is the wave vector of the photoelectron at resonance for small variation (<20%) of R. The shift of the multiple-scattering resonances with distance variation in diatomic molecules of low-Z elements has been applied in chemisorption studies but the main limitation in the bond-distance determination is in the
determination of $V$, the average interstitial potential, which is necessary for the definition of $k$ because $k$ is related to $V$ by the relation $k = \hbar \omega - E_o - \bar{V}$, where $E_o$ is the continuum threshold.

The correlation between the energy position of the multiple-scattering resonances in the continuum and the interatomic distances has been recently demonstrated by Bianconi, Natoli and others\textsuperscript{92-96}. In the framework of the $X_\alpha$-multiple-scattering theory, the absorption cross section can be shown to be determined by the multiple-scattering matrix $M$ of the photoelectron with kinetic energy $(\hbar k)^2/2m = E = E^* - \bar{V}$ where $E$ is the energy of the resonance above the threshold and $\bar{V}$ is the average muffin-tin interstitial potential as mentioned above. The maxima in the absorption correspond to the $\det(M) = 0$ condition. In this formalism, Natoli derived a relation between continuum resonance energy, $E_r$ and the first coordination shell distance,

$$ (E_r - \bar{V}) R^2 = C_r \quad (4.2) $$

where $C_r$ is the constant corresponding to $E_r$. However, $C_r$ being unknown and $\bar{V}$ being experimentally undeterminable, the above equation was found to be of little use in practice. Natoli also obtained a similar expression for the bound state resonance energy, $E_b$ with a different constant $C_b$, i.e.,

$$ (E_b - \bar{V}) R^2 = C_b \quad (4.3) $$

Combination of the two relations (4.2) and (4.3) eliminates $\bar{V}$ and leads to the following equation

$$ (E_r - E_b) R^2 = C_r - C_b \quad (4.3a) $$
This is a relation containing only measurable quantities and of immediate application.

By the term "bound or excitonic resonances" we mean those spectral pre-edge features due to transition to truly bound state in molecules (e.g., the $\pi^*$ transition in diatomic molecules\textsuperscript{97} or to antibonding states of 3d character in metal oxides\textsuperscript{94}). Both have in common the feature that they fall in an energy region where atomic resonances of the constituent atoms occur and, so to speak, are driven by them.

When applied\textsuperscript{98} to free molecules, eqn (4.3b) states that the energy difference between the $\sigma^*$ and the $\pi^*$ resonance depends only on the bond length, provided initial state differences, like more or less covalent or polarity of the bond, have the same effect on the two excited states. For chemisorbed molecules one is led to the same conclusions, provided the two resonances are affected by the metal substrate shielding in the same way. Under these assumptions\textsuperscript{98}, the constant should be transferable from one phase to another. If applied to metal oxides or in general, metal compounds, eqn (4.3b), according to Natoli\textsuperscript{98} implies that the energy separation between the pre-edge excitonic feature and the first strong absorption maximum after rising edge is a function of the bond length. The relation (4.3b) has been employed by Natoli\textsuperscript{98} and other researchers\textsuperscript{99-100} to determine the bond distances in the transition metal compounds.

The relation (4.3b) is an equation of straight line passing through the origin and having a slope $C_{rb}$. In order to determine the value of constant $C_{rb}$, we have plotted in Figure 4.9 the energy separations ($\Delta E_{3d-4p}$) between the multiple-scattering resonances in the continuum ($1s \rightarrow 4p$ transition) and bound ($1s \rightarrow$
Figure 4.9: A plot of $\Delta E_{3d-4p}$ versus $1/R^2$ for vanadium compounds
3d transition) states versus the reciprocal of square of the interatomic distances (R) for a number of vanadium compounds covering a wide range of structures. The least squares analysis of the data using all the 26 points was carried out on PC-486. As can be seen from Figure 4.9, Natoli's simple relation at first glance, does not seem to hold true for these compounds. However, when these compounds are classified according to the coordination number of vanadium and ΔE_{3d-4p} vs 1/R^2 graphs were plotted for 4-fold, 5-fold, and 6-fold coordinated compounds separately, a fairly good linear relation was found to exist between ΔE_{3d-4p} and 1/R^2 in each case as shown in Figure 4.9. For tetrahedrally coordinated compounds, the correlation coefficient and standard error of estimates are found to be 0.983 and 0.095 respectively. For penta coordinated compounds, if we take into account the data for all eight compounds for regression analysis, we get the values of correlation coefficient and standard error of estimates as 0.656 and 2.994 respectively. However, for two complexes, namely VOPc and VOTPP, the deviation for the least-squares line is very large. Such large deviations for these two compounds have also been observed in the plots of intensity of pre-edge peaks versus average bond lengths of first shell ligands in various ligand geometries in the work of Wong et al. If we perform the analysis excluding the data points for VOPc and VOTPP, the values of correlation coefficient and standard error of estimates obtained are 0.943 and 0.207 respectively. In the case of octahedrally coordinated compounds, the regression analysis gives the values of correlation coefficient and standard error of estimates as 0.747 and 1.405 respectively. By examining the experimental and calculated energy separations for the compounds, it is seen that the residues are large for VN, V_2S_3 and VC. That is why a relatively large value of standard error of estimates is obtained. However, the analysis carried out, excluding the data for VN, V_2S_3 and VC, yields the values of the correlation...
coefficient and standard error of estimates as 0.879 and 0.692 respectively. Thus, there is a lot of improvement. Although it is difficult to give any satisfactory explanation for the large deviation observed for these three compounds, the nature of bonding seems to have some role to play in the large energy separations in the X-ray absorption spectra of these compounds. For example, the V-S and V-N bonds are strongly covalent and strongly ionic in nature respectively whereas all other compounds have mixed bond character. Barring such a few exceptions, we may conclude that Natoli's relation is valid for a series of compounds wherein the metal ions have the same coordination geometry. i.e., $\Delta E_{3d-4p} x R^2 = \text{constant}$ for a particular coordination polyhedron of ligands around metal ions. The constants for tetrahedral, square pyramidal and octahedral coordination geometries were determined from the least-squares fitting of the data to a linear equation of the form $\Delta E_{3d-4p} x R^2 = C$, where $C$ is the constant for each coordination geometry and are given in Table 4.3 Once the constants are known it is easy to use this formula to predict coordination geometry and bond distance from the profiles and energy positions of the XANES peaks. We have employed this method to predict the interatomic distances in superconducting compounds for which the values of $\Delta E$ have been determined from the XANES spectra.

4.5.1 TEST OF TRANSFERABILITY OF STRUCTURAL CONSTANTS

As a first test of the transferability of these constants, we have chosen three complexes. These complexes are CrVO$_4$, (NH$_4$)$_4$[VO-dd-tart].2H$_2$O and PbV$_2$O$_6$, whose structures had been elucidated previously by X-ray crystallography$^{37,45,60}$. The absorption spectra of these two vanadium compounds were recorded and the spectra are presented in Figure 4.4. To obtain structural information, the profiles of the edges of these compounds were
compared with those of the model compounds. The comparison suggests that vanadium ions are four fold coordinated in CrVO$_4$, five-fold coordinated in (NH$_4$)$_4$[VO-dd-tart].2H$_2$O and six-fold coordinated in PbV$_2$O$_6$. Therefore using the constants $C_{\text{oct.}}$, $C_{\text{tetra}}$ and $C_{\text{spyr}}$ we have calculated the V-X (X = ligand) bond distances in the these compounds. The bond lengths 1.791 Å, 1.975 Å and 1.979 Å in CrVO$_4$, (NH$_4$)$_4$[VO-dd-tart].2H$_2$O and PbV$_2$O$_6$ respectively determined in this work are in good agreement with those reported in literature$^{37,45,60}$. The close correlation of both the coordination geometry and bond distances lends confidence to our ability to predict the coordination numbers and distances in compounds of unknown structures by XANES spectroscopy.

4.5.2 DETERMINATION OF BOND DISTANCES IN SUPERCONDUCTORS

In Figure 4.6 are shown the XANES spectra of superconducting oxides containing 2, 3, 4 and 5 percent of vanadium. As already mentioned, comparison of K-edge profiles of superconducting oxides with those of model vanadium compounds such as the presence of square-pyramidally coordinated V$^{4+}$ or V$^{5+}$ ions in these oxides. Therefore using the constant corresponding to square-pyramidal geometry, $C_{\text{spyr.}}$, we have estimated the V-0 bond distances 1.82 Å, 1.839 Å, 1.84 Å and 1.845 Å for 2, 3, 4 and 5 percent samples respectively from the energy separations 18.3, 17.9, 17.8 and 17.7 eV. Our results are in good agreement with the structural results reported by Liu and Edwards$^{75}$.

Our X-ray diffraction analysis of the samples of the series show that the structure of these oxides is similar to the TlSr$_2$CaCu$_2$O$_7$ type structure and the lattice parameter c decreases while the lattice parameter a increases with the increase of vanadium concentration. On the basis of these results we would like to suggest that the smaller V$^{4+}$ (ionic radius 0.63 Å) or
V\(^{5+}\) (ionic radius 0.59 Å) ions partially replace the larger Tl\(^{3+}\) (ionic radius 0.95 Å) sites resulting in a decrease in the lattice parameter c. In contrast, Liu and Edwards\(^7\) proposed that the partial substitution of vanadium for the thallium leads to a decrease of the hole concentration in the Cu-O plane and a corresponding increase in the lattice parameter a. However, for the confirmation of this, one has to take resort to the measurements of the normal state magnetic susceptibility of these high Tc -oxides. These results may also help to evaluate the valence state of the vanadium ion correctly.

4.6. XANES AND BOND VALENCE

The Pauling bond strengths (in valence units), referred to as bond orders or bond valences of the metal – non-metal bonds are useful in discussing the structural properties of compounds. The bond valence (s) reflects the relative strength of a chemical bond and shows the distribution of available valence electrons in the chemical bonding of a molecular species. Also, according to Pauling's valence sum rule\(^1\), there is a conservation of valency associated with the metal cation. A general relationship has been developed by Brown and Wu\(^2\)-\(^3\) that relates the cation-anion bond valence s to the interatomic distance R. The empirical expression for relating a V-O bond length to its bond valence is

\[ s_{V-O} \approx (R / 1.791)^{-5.1} \] (4.4)

where 1.791 Å is the estimated bond length for a V-O bond of unit valency. The empirical parameters in equation (4.3), 1.791 and -5.1, were determined by Brown and Wu from the data of 43 vanadium compounds having different environments\(^3\). Though this relation is given for V-O bond only, it is equally applicable for other bonds also\(^4\).
In our work we have calculated the bond valence \( (s) \) and plotted it against \( \Delta E_{3d-4p} \) for vanadium compounds in Figure 4.10. We have used few data points from the work of Sonaye\textsuperscript{69}. It is seen that, a fairly linear relationship exists between \( \Delta E_{3d-4p} \) and \( s \) for 4-fold, 5-fold and 6-fold coordinated vanadium compounds. This relationship renders the possibility of determination of bond valence in structurally unknown compounds. For example, in the superconducting oxides containing 2, 3, 4 and 5 percent vanadium, the bond valences estimated from the least-squares analysis of the data on \( \Delta E_{3d-4p} \) and \( s \) are found to be and 0.892, 0.848, 0.837 and 0.826 respectively indicating that the vanadium ions are in \( 4^+ \) or \( 5^+ \) state.

It is interesting to mention here that in Raman spectroscopy correlations between vanadium-oxygen bond valence and vanadium-oxygen stretching frequencies have been shown and fruitfully used\textsuperscript{103} for the determination of oxidation states in compounds in complicated oxide systems such as vanadium oxides supported on alumina and titania substrates. In EXAFS spectroscopy also, such correlations have been used\textsuperscript{63} to estimate the bond valence from the distances determined from the Fourier transform analysis of the EXAFS spectra.
Figure 4.10: A plot of $\Delta E_{3d-4p}$ versus bond valence (s) for vanadium compounds
REFERENCES


57. M. Marezio, D.B. Mowhan, P.D. Dernier and J.P. Remeika, J.
92. A. Bianconi, in EXAFS and Near Edge Structure eds. A.


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Table 4.1. ENERGY POSITIONS OF VARIOUS SPECTRAL FEATURES IN VANADIUM K-EDGE SPECTRA IN VANADIUM COMPOUNDS

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Absorber</th>
<th>Pre-edge peak (eV) 1s→3d</th>
<th>Main Absorption peak (eV) 1s→4p</th>
<th>Energy separation ΔE_{3d-4p} (eV)</th>
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<td>V metal *</td>
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<td>19.3</td>
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<tr>
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<td>CrVO₄ ¹</td>
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</tr>
<tr>
<td>3.</td>
<td>GdVO₄</td>
<td>3.9</td>
<td>24.7</td>
<td>20.8</td>
</tr>
<tr>
<td>4.</td>
<td>BiVO₄</td>
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<td>26.4</td>
<td>21.7</td>
</tr>
<tr>
<td>5.</td>
<td>Cd₂V₂O₇</td>
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</tr>
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<td>% Loss</td>
<td>Temp. (°C)</td>
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* Test compounds
+ Data taken from unpublished work of B. H. Sonaye
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<th>No. of Bonds</th>
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<th>s&lt;sup&gt;c&lt;/sup&gt;</th>
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<tr>
<td>17.</td>
<td>VO(SO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4</td>
<td>V-O</td>
<td>5</td>
<td>1.936</td>
<td>0.672</td>
<td>49(b)</td>
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<td>18.</td>
<td>VO(acen)</td>
<td>4</td>
<td>V-O</td>
<td>5</td>
<td>1.922</td>
<td>0.698</td>
<td>49(c)</td>
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</table>

Coordination Polyhedron: Tetrahedron

Coordination Polyhedron: Square pyramid

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Coordination Polyhedron: Octahedron

<table>
<thead>
<tr>
<th></th>
<th>Oxidation state</th>
<th>Bond distance</th>
<th>Bond valence</th>
<th></th>
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<tbody>
<tr>
<td>19</td>
<td>VO</td>
<td>V-O</td>
<td>6</td>
<td>2.050</td>
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<tr>
<td>20</td>
<td>(NH₄)₂SO₄VSO₄·6H₂O</td>
<td>V-O</td>
<td>6</td>
<td>2.140</td>
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<tr>
<td>21</td>
<td>V₂O₃</td>
<td>V-O</td>
<td>6</td>
<td>2.010</td>
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<td>22</td>
<td>SmVO₃</td>
<td>V-O</td>
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<td>23</td>
<td>V₂S₃</td>
<td>V-S</td>
<td>6</td>
<td>2.080</td>
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<td>24</td>
<td>VN</td>
<td>V-N</td>
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<td>2.070</td>
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<tr>
<td>25</td>
<td>VO₂</td>
<td>V-O</td>
<td>6</td>
<td>1.930</td>
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<tr>
<td>26</td>
<td>V₄O₇</td>
<td>V-O</td>
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<tr>
<td>27</td>
<td>VC</td>
<td>V-C</td>
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<td>2.091</td>
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<td>28</td>
<td>[VO(hshed)(acac)]</td>
<td>V-O</td>
<td>6</td>
<td>1.973</td>
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<tr>
<td></td>
<td></td>
<td>V-N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>PbV₂O₆</td>
<td>V-O</td>
<td>6</td>
<td>1.962</td>
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<tr>
<td>30</td>
<td>Ca₃V₁₀O₂₈·16H₂O</td>
<td>V-O</td>
<td>6</td>
<td>1.920</td>
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<td>31</td>
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<td>(5)</td>
<td>1.730</td>
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<td>32</td>
<td>3 % sample</td>
<td>(5) V-O</td>
<td>(5)</td>
<td>1.798</td>
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<tr>
<td>33</td>
<td>4 % sample</td>
<td>(5) V-O</td>
<td>(5)</td>
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<tr>
<td>34</td>
<td>5 % sample</td>
<td>(5) V-O</td>
<td>(5)</td>
<td>1.847</td>
</tr>
</tbody>
</table>

a Q = Oxidation state  
b R = Bond distance  
c s = Bond valence  
d Trigonal prismatic complex
### TABLE 4.3. VALUES OF STRUCTURAL CONSTANTS

<table>
<thead>
<tr>
<th>Coordination polyhedron</th>
<th>Notation for the constant</th>
<th>Numerical Value of the constant</th>
</tr>
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<tbody>
<tr>
<td>Tetrahedron</td>
<td>$C_{tetra}$</td>
<td>64.46</td>
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<tr>
<td>Square Pyramid</td>
<td>$C_{sq.pyr}$</td>
<td>61.08</td>
</tr>
<tr>
<td>Octahedron</td>
<td>$C_{oct}$</td>
<td>77.62</td>
</tr>
</tbody>
</table>