CHAPTER - VII
ELECTRON PARAMAGNETIC RESONANCE STUDY
OF VANADYL ION IN BARIUM FORMATE *

7.1 INTRODUCTION

Electron Paramagnetic Resonance (EPR) studies of transition metal complexes give valuable information about the nature of the bonding of the central metal ion with the ligands. The bonding parameters are contained in the expressions for the spin-Hamiltonian constants which describe the resonance spectra. One uses in this context a linear combination of atomic orbitals-molecular orbital (LCAO-MO). In recent years vanadyl ion has been the subject of a number of studies [1-4]. The behaviour of the unpaired electron in vanadyl complexes is dominated by the strong V=O bonding and most of the complexes possess square pyramid symmetry ($C_{4v}$) and both $\hat{g}$ and $\hat{A}$ tensors are found to be axially symmetric. However, in some cases the ligand field symmetry was found to be reduced [5]. Probably, there is no EPR work on vanadyl doped barium formate and in this Chapter we are reporting the results of EPR and optical studies of vanadyl ion in barium formate in which the MO bonding coefficients and crystal field parameters have been calculated and discussed.

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The crystal structure of barium formate has already been described in the last chapter.

7.2 EXPERIMENTAL DETAILS

A weighed amount of barium carbonate was neutralized with formic acid and crystals were grown from aqueous solution by isothermal evaporation at 300 K. A very little amount of \( \text{VOS}_4 \cdot 5\text{H}_2\text{O} \) was added to the stock solution for the purpose of doping. A little greater amount of the impurity impedes crystal growth. After addition of \( \text{VOS}_4 \cdot 5\text{H}_2\text{O} \), the solution becomes unclear probably due to the formation of \( \text{BaSO}_4 \). A clear solution is obtained on filtering the solution several times. This clear solution was allowed to evaporate under isothermal condition and colourless transparent crystals with well developed faces were recovered. All the chemicals used were "pro analysi" grade.

The optical absorption spectrum was recorded at RT on a spectrophotometer (model Pye Unicam PU8800) in the range 300 to 900 nm. The EPR spectrum was recorded on an X-band (~9.4 GHz) EPR spectrometer (Varian model E-109) with 100 kHz field modulation. Due to some experimental constraints, the EPR was studied only in polycrystalline phase.
7.3 THEORY

The VO\(^{2+}\) ion has the electronic configuration [Ar]\(^{18}\)3d\(^{1}\). In crystal field of octahedral symmetry, the d\(^{1}\) electron occupies the lowest t\(_{2g}\) orbital and gives rise to the ground state \(^{2}T\(_{2g}\)\). In the excited state the electron occupies the upper e\(_{g}\) orbital and gives rise to a \(^{2}E\(_{g}\)\) state. Thus only one band corresponding to \(^{2}T\(_{2g}\) \rightarrow ^{2}E\(_{g}\)\) transition is expected. However, in tetragonal field C\(_{4v}\), the \(^{2}T\(_{2g}\)\) state splits into \(^{2}B\(_{2}\)\) and \(^{2}E\) and \(^{2}E\(_{g}\)\) state splits into \(^{2}B\(_{1}\)\) and \(^{2}A\(_{1}\)\). The relative positions of the energy levels [6] are shown in Fig. 7.1. To confirm the absence of water of crystallization the IR spectrum was also recorded and is shown in Fig. 7.2.

7.4 RESULTS AND DISCUSSION

Figure 7.3 shows the optical absorption spectrum recorded at RT. The spectrum shows two bands, one intense band centred at 12050 cm\(^{-1}\) and another weak band at 16260 cm\(^{-1}\). These two bands are assigned to the \(^{2}B\(_{2}\) \rightarrow ^{2}E\) and \(^{2}B\(_{2}\) \rightarrow ^{2}B\(_{1}\)\) transitions respectively [6,7]. From the transition \(^{2}B\(_{2}\) \rightarrow ^{2}B\(_{1}\)\) octahedral (Dq) crystal field parameter comes out to 1626 cm\(^{-1}\). The values of tetrahedral (Ds, Dt) crystal field parameters can be calculated by making the reasonable assumption that the \(^{2}B\(_{2}\) \rightarrow ^{2}A\(_{1}\)\) transition for VO\(^{2+}\) ion occurs at approximately
Fig. 7.1 Energy level splittings for d$^1$ configuration in octahedral and tetragonal fields.
Fig. 7.2 Infrared spectrum of $\text{VO}^{2+}$ doped barium formate.
Fig. 7.3 Optical absorption spectrum of VO$^{2+}$ in barium formate.
35000 cm$^{-1}$ (this transition is observed in number of vanadyl complexes in the neighbourhood of 30000 cm$^{-1}$) [6]. This calculation gives $D_s = -4398$ cm$^{-1}$ and $D_t = -229$ cm$^{-1}$.

The EPR spectrum of the polycrystalline sample recorded at RT is shown in Fig. 7.4. There are two obvious points. First, all of the single crystal sites have probably the same spin-Hamiltonian parameters, since there is only one set of lines (consisting of parallel and perpendicular components) in the powder spectrum. Secondly, the absence of any small splitting in the perpendicular components of the spectrum indicates that all sites have axial symmetry. If at all there is any rhombic distortion, its effect is smaller than the line-width. In this case the spin-Hamiltonian parameters can be determined from the experimental spectrum using the equations [8]

$$B_{\|}(m) = B_{\|} - \frac{A_{\|} m}{g_{\|} \beta} - \frac{A_{\perp}^2}{2(g_{\|}^2 \beta^2 B_{\|})} [I(I+1)-m^2] \quad (7.1)$$

and

$$B_{\perp}(m) = B_{\perp} - \frac{A_{\perp} m}{g_{\perp} \beta} - \frac{A_{\|}^2 + A_{\perp}^2}{4(g_{\|}^2 \beta^2 B_{\|})} [I(I+1)-m^2] \quad (7.2)$$

which are obtained by evaluating the general second order perturbation expression for the resonance magnetic field at $\Theta=0^\circ$ and $\Theta=90^\circ$ respectively. The values determined are:
Fig. 7.4 EPR spectrum of $\text{VO}^{2+}$ ion in barium formate at room temperature in polycrystalline phase.
The Fermi contact term and the molecular orbital coefficients are estimated from the following expressions [9,10]

\[
A_{\parallel} = P\left[-\beta_2^2 \left(\frac{4}{7} + k\right) + (g_{\parallel} - g_e) + \frac{3}{7} (g_{\perp} - g_e)\right]
\]

\[
A_{\perp} = P\left[\beta_2^2 \left(\frac{2}{7} - k\right) + \frac{11}{14} (g_{\perp} - g_e)\right]
\]

where \(g_e = 2.0023\) and \(\beta_2^2\) is taken as unity [9]. Substituting the values of \(g_{\parallel}, g_{\perp}, A_{\parallel}\) and \(A_{\perp}\) evaluated from the EPR spectrum in the above equations, we get,

\[
P = -121 \times 10^{-4} \text{ cm}^{-1}
\]

and \(k = 0.79\)

The optical and EPR data can be correlated to determine the molecular orbital coefficients and these coefficients are evaluated from [3,10]

\[
g_{\parallel} = 2.0023 - \frac{8\lambda \beta^2}{\Delta_{\parallel}},
\]

\[
g_{\perp} = 2.0023 - \frac{2\lambda \varepsilon^2}{\Delta_{\perp}},
\]

\[
A_{\parallel} = P\left[-\left(\frac{4}{7} + k\right) - \frac{8(\lambda \beta^2)}{\Delta_{\parallel}} - \frac{6}{7} \frac{(\lambda \varepsilon^2)}{\Delta_{\perp}}\right],
\]

\[
A_{\perp} = \frac{0}{0}
\]
and

\[ A_\perp = P \left[ \left( \frac{2}{7} - k \right) - \frac{11(\lambda \varepsilon^2)}{7 \Delta_\perp} \right] \]  

(7.8)

where \( \beta^2 \) and \( \varepsilon^2 \) are the fractional contributions of the wave functions in the orbitals \( |x^2-y^2\rangle \) and \((|xz\rangle, |yz\rangle)\) respectively, \( \lambda \) is the spin-orbit coupling coefficient which is assumed to be equal to \(-170 \text{ cm}^{-1} \) for \( \text{V}^2+ \) ion [9], \( k \) is the Fermi contact parameter and is related to the unpaired electron density at the vanadium nucleus, \( \Delta_\perp \) and \( \Delta_\parallel \) are the energy separations between ground state \( (^2B_2) \) and the next higher states \( (^2E \text{ and } ^2B_1) \) respectively. The parameter 'P' is a measure of the radial distribution of the unpaired electron wave functions and is given by

\[ P = 2.0023 g_N \beta_N \langle r^{-3} \rangle \]  

(7.9)

Inserting the experimental values of \( g_\parallel \), \( g_\perp \), \( \Delta_\parallel \) and \( \Delta_\perp \) in eqns.(7.7 and 7.8), the values of the molecular orbital coefficients evaluated are \( \beta^2 = 0.81 \) and \( \varepsilon^2 = 0.79 \) respectively. Solving eqns.(7.7 and 7.8) the value of \( k \) is found to be 0.79 (as has been calculated by eqns.(7.3 and 7.4)). The parameters \( \beta^2 \) and \( \varepsilon^2 \) represent in-plane(\( \sigma \)) and out-of-plane(\( \pi \)) bonding respectively.
7.5 CONCLUSIONS

The large value of \( k \) indicates a large contribution to the hyperfine splitting constant by the unpaired \( S \)-electron and probably also the contribution from spin polarization. The value of \( \beta^2 \) gives an indication of the degree of covalency in the \( b_2 \) orbital. Ballhausen and Gray [6] pointed out that the value of \( \beta^2 \) should be equal to unity as this orbital is a non-bonding orbital in case of pure \([\text{VO(H}_2\text{O)}_5]^2+\) complex.

One can see that the value of \( \beta^2 \) is nearer to unity. The deviation of \( \beta^2 \) from unity indicates a degree of admixture of the ligand orbitals. This must be due to the particular type of ligands available in the lattice and also due to the low symmetry of the ligand field which is indeed the case [4].
REFERENCES


