Theoretical studies of the optical spectra and EPR parameters for VO$^{2+}$ ions in Zn(antipyrine)$_2$(NO$_3$)$_2$

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Abstract

The optical spectrum band positions and EPR parameters ($g$ factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$ and $A_\perp$) for VO$^{2+}$ ions in Zn(antipyrine)$_2$(NO$_3$)$_2$ are theoretically studied from the complete diagonalization (of energy matrix) method (CDM) and the perturbation theory method (PTM). In the two methods, the contributions from the spin–orbit (SO) coupling of central 3d$^n$ ion and ligand are taken into account. The theoretical results from both methods are not only consistent with the experimental values, but also close to each other. The results are discussed.

Keywords: Electron paramagnetic resonance (EPR); Crystal-fields and Spin Hamiltonians; VO$^{2+}$; Zn(antipyrine)$_2$(NO$_3$)$_2$

1. Introduction

Vanadyl ion (VO$^{2+}$) as the most stable cation among the molecular paramagnetic transition metal ions has been extensively used as a probe to study local structures and properties in doped crystals by means of Electronic paramagnetic resonance technique [1-8]. The VO$^{2+}$ ion has the electronic configuration [Ar] 3d$^1$ and the single unpaired spin leads to paramagnetism in VO$^{2+}$. The behavior of the unpaired electron in VO$^{2+}$ complexes is dominated by the strong V=O bond, as a result most of the complexes possess tetragonal symmetry with both $g$ and $A$ values found to be axially symmetric. This is supported by many EPR experiments [9-13]. For example, Sreeramachandra has studied the EPR and optical spectra of VO$^{2+}$ ion in Zn(antipyrine)$_2$(NO$_3$)$_2$ crystal [3], and the EPR parameters ($g_\parallel$, $g_\perp$, $A_\parallel$, $A_\perp$) were obtained. Until now, however, these experimental results have not been satisfactorily interpreted. In order to investigate the observed results for the VO$^{2+}$ ion in Zn(antipyrine)$_2$(NO$_3$)$_2$ crystal to a good extent, two methods are applied: one is the perturbation theory method (PTM), the other is the complete diagonalization (of energy matrix) method (CDM). In the two methods, the contributions from the p- and s-orbitals as well as the spin-orbit coupling of the ligands are taken into account. The results are discussed.

2. Calculations

2.1. calculation by using the diagonalization of energy matrix(CDM)

From crystal- and ligand-field theory, the single electron basis function for an octahedral 3d$^n$ cluster can be written as [14, 15]

$$\psi_{\gamma} = N_{\gamma}^{1/2} \left( \phi_{\gamma} - \lambda_{\gamma} \chi_{\gamma} \right)$$

$$\psi_{\gamma} = N_{\gamma}^{1/2} \left( \phi_{\gamma} - \lambda_{\gamma} \chi_{\gamma} - \lambda_{\gamma} \chi_{\gamma} \right)$$

(1)

where $\phi_{\gamma}$ (the subscript $\gamma$=e or t stands for the irreducible representation of O$_h$ group) is the d-orbital of the central 3d$^n$ ion, $\chi_{\gamma}$ and $\chi_{\gamma}$ are the p-orbital and s-orbital of ligand. $N_\gamma$ and $\lambda_\gamma$ (or $\lambda_\gamma$) are, respectively, the normalization factors and the orbital mixing coefficients. The normalization relationship can be given as [16]:

$$N_{\gamma} (1 - 2 \lambda_\gamma S_{d\gamma} + \lambda_\gamma^2) = 1$$

$$N_{\gamma} (1 - 2 \lambda_\gamma S_{d\gamma} - 2 \lambda_\gamma S_{s\gamma} + \lambda_\gamma^2 + \lambda_\gamma^2) = 1$$

(2)

and the approximate relationships [16]

$$N^2 = N^2_{\gamma} [1 + \lambda_\gamma^2 S_{d\gamma}^2 - 2 \lambda_\gamma S_{d\gamma}]$$

$$N^2 = N^2_{\gamma} [1 + \lambda_\gamma^2 S_{d\gamma}^2 + \lambda_\gamma^2 S_{s\gamma}^2 + 2 \lambda_\gamma S_{d\gamma} S_{s\gamma} - 2 \lambda_\gamma S_{s\gamma}]$$

(3)

Here, $N$ is the average covalency factor, characteristic of the covalency effect (or reduction of the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter) of the central
ion in crystals. \( S_{\text{dp}} \) (and \( S_{\text{d}} \)) are the group overlap integrals. In general, the mixing coefficients increase with increasing the group overlap integrals, and one can approximately adopt proportionality between the mixing coefficients and the related group overlap integrals, i.e., \( \lambda_{\text{e}} / S_{\text{dpp}} \approx \lambda_{\text{e}} / S_{\text{dp}} \), within the same irreducible representation \( \eta_{\text{p}} \).

Thus, the spin-orbit coupling coefficients and the orbital reduction factors can be written as:

\[
\zeta = N_{1}(\zeta_{\text{d}} + \lambda_{\text{e}} \zeta_{\text{p}} / 2)
\]

\[
\zeta' = (N_{1}N_{2})^{1/2}(\zeta_{\text{d}} - \lambda_{\text{e}} \zeta_{\text{p}} / 2)
\]

\[
k = N_{1}(1 + \lambda_{\text{e}} / 2)
\]

\[
k' = (N_{1}N_{2})^{1/2}[1 - \lambda_{\text{e}}(\lambda_{\text{e}} + \lambda_{\text{a}})/4]
\]

(4)

where \( \zeta_{\text{d}} \) and \( \zeta_{\text{p}} \) are the spin-orbit coupling coefficients of the 3d\(^{n}\) and ligand ions in free states, respectively. \( A \) denotes the integral \( R_{\text{p}}(\pi_{\text{p}} / 2 \pi_{\text{p}}) \), where \( R \) is the impurity ligand distance in the studied system.

The Hamiltonian for the d\(^{1}\) ion in crystal-field can be written as [14]

\[
g_{e} = 2<\Phi^{+} | L_{z} + g_{e} S_{z} | \Phi^{-}> = 4(2c_{3}c_{5}k - c_{2}c_{1}k) + g_{e}(1 - 2c_{2}^{2} - 2c_{1}^{2})
\]

\[
g_{g} = 2<\Phi^{-} | L_{z} + g_{e} S_{z} | \Phi^{+}> = -2(2\sqrt{3} c_{1}c_{2}k + 2c_{2}c_{3}k - 2c_{1}c_{2}k) + ge(2c_{2}^{2} + 2c_{1}^{2} - 1)
\]

(6)

where \( g_{e}(=2.0023) \) is the spin-only value, \( k' \) and \( k \) are the orbital reduction factors as mentioned in Eq.(4). \( \lambda_{\text{e}}(\lambda_{\text{e}}) \) and \( S_{\text{d}}(S_{\text{e}}) \) are the orbit and spin angular momentums, respectively. The constants \( A_{g} \) and \( A_{e} \) are related to the g factors. They can be written as:

\[
A_{e} = P(-\kappa - 4N_{e}^{7/4}(g_{e} - g_{e}) + 3(g_{e} - g_{e})/7)
\]

\[
A_{g} = P(-\kappa + 2N_{e}^{7/4} + 11(g_{e} - g_{e})/14)
\]

(7)

where \( P \) is the dipolar hyperfine structure parameter of the free 3d\(^{1}\) ion. \( \kappa \) is the isotropic core polarization constant. For the free \( V^{4+} \) and \( O^{2-} \) ions, we have \( \zeta_{e} \approx 284 \text{ cm}^{-1} \) [17] \( P \approx 136 \times 10^{4} \text{ cm}^{-1} \) [18] for \( V^{4+} \) and \( \zeta_{p} \approx 151 \text{ cm}^{-1} \) [19] for \( O^{2-} \) respectively. The group overlap integrals \( S_{\text{dp}} \) (and \( S_{\text{d}} \)) can be calculated from the Slater-type self-consistent field (SCF) functions [20, 21] with the impurity-ligand distance \( R \). For the present system, the impurity-ligand length is unknown, but the V-O bond length (\( \approx 0.195 \text{nm} \)) is obtained for VO\(^{2+}\) in cubic field [22], and we take \( R = 0.195 \text{nm} \) here. Thus the group overlap integrals which are shown in Table 1 can be calculated. Substituting the above parameters to the equations (2) (3) (4), the spin-orbit coupling coefficients \( (\zeta, \zeta') \) the normalization factors \( (N_{1}) \) and the orbital mixing coefficients \( (\lambda_{\text{e}}, \lambda_{\text{a}}) \) can be obtained, and are shown in Table 1.

The unknown parameters \( N_{1}, \kappa, D_{0}, D_{g}, D_{e} \) can be obtained by fitting the calculated optical and EPR spectra data to the observed values. We have

\[ N \approx 0.886, \kappa = 0.698, D_{0} \approx 2141 \text{ cm}^{-1}, \]

\[ D_{g} \approx 3010 \text{ cm}^{-1}, D_{e} \approx 1645 \text{ cm}^{-1}. \]

The calculated three optical spectrum band positions and four EPR parameters are compared with the experimental values [3] in Table 2.

2.2. Calculation using the high order perturbation approach (PTM)

For a 3d\(^{1}\)(VO\(^{2+}\)) ion in tetragonally distorted octahedra, its higher orbital doublet \( ^{2}E_{g} \) of the original cubic case would split into two orbital singlets \( ^{2}A_{1} \) (0) and \( ^{2}B_{1} \)(e), while the original lower orbital triplet \( ^{2}T_{2g} \) would be separated into an orbital singlet \( ^{2}B_{2}(\zeta) \) and a doublet \( ^{2}E(\eta, \xi) \) [23], with the former lying lowest for the present system [3].

By using the perturbation procedure similar to that of Pilbrow and Gourier [24, 25], the two SO coupling coefficient formulas of the g factors for a 3d\(^{1}\) ion under octahedral tetragonal symmetry can be obtained from the cluster approach:

\[
g_{e} = g_{e} - 8k_{\zeta}^{2}/E_{2} - 2k_{\zeta}^{2}/E_{2} + 2k_{\zeta}^{2}/E_{2}
\]

\[
g_{g} = g_{e} - 2k_{\zeta}^{2}/E_{2} + 2k_{\zeta}^{2}/E_{2} + 1/E_{2} - 1/E_{1}
\]

(8)

The energy denominators \( E_{1} \) and \( E_{2} \) stand for the energy separations between the excited \( ^{2}B_{1} \), \( ^{2}E \) and the ground \( ^{2}B_{2} \) states. They can be expressed in
terms of the tetragonal field parameters $D_s$ and $D_t$ and the cubic field parameter $D_q$

$$E_1 = 10D_q$$
$$E_2 = -3D_s + 5D_t$$

(9)

Applying the same parameters ($D_\alpha$, $D_\beta$, $D_\gamma$) (obtained by CDM) to the above equations, the optical spectrum band positions are calculated and shown in Table 2. Substituting the above energy differences $E_1$, $E_2$ and using the same parameters $N$, $\kappa$ (obtained by CDM) to Eq.(8) and then to Eq.(7), the EPR parameters $g_\perp$, $g_\parallel$, $A_\perp$, $A_\parallel$ are calculated and also shown in Table 2.

3. Discussion

From Table 2, one can find that the calculated optical band positions and EPR parameters from two methods (CDM and PTM) including the ligand orbital and spin-orbit coupling contributions are not only very close to each other but also in keeping with the observed values. This suggests that both microscopic Spin Hamiltonians approaches based on the two-SO-parameters model are effective in the theoretical investigations of EPR parameters for 3d$^1$ ion in crystals.

(1) The calculated results based on the complete diagonalization (of energy matrix) method (CDM) and the higher perturbation formulas in equation (8) of the present work are better than those (Cal.$^a$ in Table 2) based on the simple formulas neglecting the contributions from the ligand orbitals. Owing to the high valence state of V$^{4+}$, moderate covalency (or admixture) between the metal and ligand orbitals can be expected. This point is illustrated by the small covalency factor $N$ ($=0.886<1$) in equation (3) and the moderate mixing coefficients (see Table 1) obtained from the cluster approach. Meanwhile, the ratio $(\zeta^2+\zeta)/2\zeta (=0.91)$ and the average $(\kappa/k)$ $/2 (=0.89)$ in the present work, approximately account for the covalency effect. This point may be illustrated by the comparable optical electronegativity ($\approx 2.6$) for V$^{4+}$ with ($\approx 3.2$) for O$^-$ [26], as an indication of moderate covalency for this metal-ligand combination. Therefore, the formulas of the EPR parameters containing the ligand orbital and spin-orbit coupling contributions seem to be more applicable than the simple ones in the absence of these contributions for the investigations on the EPR parameters of impurity ions in covalent systems.

Table 1. The group overlap (and $A$) integrals, molecular orbital coefficients $N_\alpha$ and $\lambda_\alpha$ (and $\lambda_\alpha$), spin-orbit coupling coefficients (in cm$^{-1}$) and the orbital reduction factors for VO$^{2+}$ in Zn (antipyrine)$_2$(NO$_3$)$_2$

<table>
<thead>
<tr>
<th>$\lambda_\alpha$</th>
<th>$\lambda_\alpha$</th>
<th>$\lambda_\alpha$</th>
<th>$\lambda_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05082</td>
<td>0.12904</td>
<td>0.10063</td>
<td>1.01018</td>
</tr>
<tr>
<td>$N_\alpha$</td>
<td>$N_\alpha$</td>
<td>$N_\alpha$</td>
<td>$N_\alpha$</td>
</tr>
<tr>
<td>0.4324</td>
<td>0.2736</td>
<td>234.0019</td>
<td>22.25665</td>
</tr>
<tr>
<td>$A_\parallel$</td>
<td>$A_\parallel$</td>
<td>$A_\perp$</td>
<td>$A_\perp$</td>
</tr>
<tr>
<td>0.9335</td>
<td>0.9355</td>
<td>0.3815</td>
<td>0.3815</td>
</tr>
</tbody>
</table>

Table 2. The optical spectrum band positions (in cm$^{-1}$) and EPR parameters for VO$^{2+}$ ions in Zn (antipyrine)$_2$(NO$_3$)$_2$

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Expt$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{3}\text{B}_2 \rightarrow ^{5}\text{E}$</td>
<td>17220/17270</td>
</tr>
<tr>
<td>$^{3}\text{B}_2 \rightarrow ^{5}\text{B}_1$</td>
<td>21474/21283</td>
</tr>
<tr>
<td>$^{3}\text{B}_2 \rightarrow ^{5}\text{A}_1$</td>
<td>25212/25427</td>
</tr>
</tbody>
</table>

$^a$Calculations by using the high-order perturbation formulas in equation (8) and (7) but neglecting the ligand orbital contributions (i.e., taking $\zeta_\alpha=\zeta=N\zeta_\alpha$ and $k=k'=N$).

$^b$Calculations by using the high-order perturbation formulas in equation (8) and (7) and including the ligand orbital contributions.

$^c$Calculations by using CDM in this work.

(2) Many studies show that the core polarization $\kappa$ in various V$^{4+}$ (or VO$^{2+}$) clusters in crystals is in the range 0.6-1.0 [27, 28, 29]. The value $\kappa=0.698$ obtained in this work is within the range and can be regarded as rational.

(3) The observed values of $A_\parallel$ and $A_\perp$ from the EPR experiment given by Sreekumaran and Subramanian are positive [3]. However, the theoretical calculations are negative (see Table 2). In fact, these negative signs of the hyperfine structure constants are supported by the experimental results for many octahedral VO$^{2+}$ or V$^{4+}$ clusters in various crystals [30, 31]. As for the magnitudes of the hyperfine structure contents, the smaller values ($A_\parallel \approx 171 \times 10^{-4} \text{cm}^{-1}$ and $A_\perp \approx 65.9 \times 10^{-4} \text{cm}^{-1}$) for the studied system than those ($A_\parallel \approx 182.8 \times 10^{-4} \text{cm}^{-1}$ and $A_\perp \approx 72.0 \times 10^{-4} \text{cm}^{-1}$ for VO($\text{H}_2\text{O}$)$_2$) [32]) for some VO$^{2+}$ doped oxides are usually ascribed to the covalency of the system, as mentioned for many transition-metal complexes. So, the above calculated $A_\parallel$ and $A_\perp$ are reasonable in sign and in magnitude.

4. Conclusions

In this paper, the contributions from the ligand orbitals and spin-orbit coupling interactions are considered in the theoretical investigations of the EPR parameters for the VO$^{2+}$ ions in Zn (antipyrine)$_2$(NO$_3$)$_2$ and the theoretical EPR parameters based on the above contributions in this work are in good agreement with the experimental data.

References


