

Theoretical studies of the optical spectra and EPR parameters for VO²⁺ ions in Zn(antipyrine)₂(NO₃)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 VO²⁺ ions in Zn(antipyrine)₂(NO₃)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 3dⁿ 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; VO²⁺; Zn(antipyrine)₂(NO₃)₂

1. Introduction

Vanadyl ion (VO²⁺) 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 VO²⁺ ion has the electronic configuration [Ar] 3d¹ and the single unpaired spin leads to paramagnetism in VO²⁺. The behavior of the unpaired electron in VO²⁺ 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 VO²⁺ ion in Zn(antipyrine)₂(NO₃)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 VO²⁺ ion in Zn(antipyrine)₂(NO₃)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 3dⁿ cluster can be written as [14, 15]

$$\begin{aligned}\psi_t &= N_t^{1/2} (\varphi_t - \lambda_t \chi_{pt}) \\ \psi_e &= N_e^{1/2} (\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s)\end{aligned}\quad (1)$$

where φ_{γ} (the subscript $\gamma=e$ or t stands for the irreducible representation of O_h group) is the d-orbital of the 3dⁿ ion. $\chi_{p\gamma}$ and χ_s are the p-orbital and s-orbital of ligand. N_{γ} and λ_{γ} (or λ_s) are, respectively, the normalization factors and the orbital mixing coefficients. the normalization relationship can be given as [16]:

$$\begin{aligned}N_t (1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1 \\ N_e (1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1\end{aligned}\quad (2)$$

and the approximate relationships [16]

$$\begin{aligned}N^2 &= N_t^2 [1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}] \\ N^2 &= N_e^2 [1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}]\end{aligned}\quad (3)$$

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_{dpy} (and S_{ds}) 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., $\lambda_e / S_{dpe} \approx \lambda_s / S_s$ within the same irreducible representation e_g . Thus, the spin-orbit coupling coefficients and the orbital reduction factors can be written as:

$$\begin{aligned} \zeta &= N_t (\zeta_d + \lambda_t^2 \zeta_p / 2) \\ \zeta' &= (N_t N_e)^{1/2} (\zeta_d - \lambda_t \lambda_e \zeta_p / 2) \\ k &= N_t (1 + \lambda_t^2 / 2) \\ k' &= (N_t N_e)^{1/2} [1 - \lambda_t (\lambda_e + \lambda_s A) / 2] \end{aligned} \quad (4)$$

where ζ_d and ζ_p are the spin-orbit coupling coefficients of the $3d^n$ and ligand ions in free states, respectively. A denotes the integral $R \langle n_s | \frac{\partial}{\partial y} | n p_y \rangle$, 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]

$$\begin{aligned} g_{//} &= 2 \langle \Phi^+ | L_z + g_e S_z | \Phi^+ \rangle = 4(2c_3 c_5 k' - c_2 c_1 k) + g_e (1 - 2c_2^2 - 2c_1^2) \\ g_{\perp} &= 2 \langle \Phi^+ | L_x + g_e S_x | \Phi^+ \rangle = 2(-2\sqrt{3} c_1 c_4 k' + 2c_3 c_2 k - 2c_1 c_5 k') + g_e (2c_3^2 + 2c_2^2 - 1) \end{aligned} \quad (6)$$

where $g_e (\approx 2.0023)$ is the spin-only value, k' and k are the orbital reduction factors as mentioned in Eq.(4). $L_z (L_x)$ and $S_z (S_x)$ are the operators of orbit and spin angular momentums, respectively. The constants $A_{//}$ and A_{\perp} are related to the g factors. They can be written as:

$$\begin{aligned} A_{//} &= P[-\kappa - 4N^2/7 + (g_{//} - g_s) + 3(g_{\perp} - g_s)/7] \\ A_{\perp} &= P[-\kappa + 2N^2/7 + 11(g_{\perp} - g_s)/14] \end{aligned} \quad (7)$$

where P is the dipolar hyperfine structure parameter of the free $3d^1$ ion. κ is the isotropic core polarization constant. For the free V^{4+} and O^{2-} ions, we have $\zeta_d \approx 248 \text{ cm}^{-1}$ [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_{dpy} (and S_{ds}) 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 $R \approx 0.195 \text{ nm}$ 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 (ζ, ζ') the normalization factors (N_t) and the orbital mixing coefficients (λ_t, λ_s) can be obtained, and are shown in Table 1. The unknown parameters N, κ, D_q, D_s, D_t , can be obtained by fitting the calculated optical and EPR

$$H = H_f + H_{so}(\zeta, \zeta') + H_{CF}(D_q, D_s, D_t)$$

where H_f is the free-ion Hamiltonian. $H_{so}(\zeta, \zeta')$ is the spin-orbit coupling interactions including two SO coupling parameters ζ and ζ' . H_{CF} is the crystal-field Hamiltonian for $3d^1$ ion in tetragonal symmetry. By using the strong field basis functions in tetragonal symmetry, the 10×10 complete Hamiltonian matrix elements of the crystal field and spin-orbit coupling based on the two-SO-parameter model are obtained. Diagonalizing the energy matrix, the eigenvalues (hence the energy levels and the optical spectrum band positions) and the wave functions of the ground state can be obtained. For the spin doublet ground state, we have the wave function:

$$\begin{aligned} |\Phi^+ \rangle &= c_1 |\psi_{\xi}^- \rangle + c_2 |\psi_{\eta}^- \rangle + c_3 |\psi_{\zeta}^+ \rangle + c_4 |\psi_{\theta}^+ \rangle + c_5 |\psi_{\epsilon}^+ \rangle \\ |\Phi^- \rangle &= c_1 |\psi_{\xi}^+ \rangle + c_2 |\psi_{\eta}^+ \rangle + c_3 |\psi_{\zeta}^- \rangle - c_4 |\psi_{\theta}^- \rangle - c_5 |\psi_{\epsilon}^- \rangle \end{aligned} \quad (5)$$

where ψ is the LCAO molecular-orbitals for a $3d^1$ ion in octahedra based on the cluster approach (see Eq. (1)). Considering the equivalence between the SH and Zeeman interaction, the g factors are:

spectra data to the observed values. We have

$$\begin{aligned} N &\approx 0.886, \kappa \approx 0.698, D_q \approx 2141 \text{ cm}^{-1}, \\ D_s &\approx -3010 \text{ cm}^{-1}, D_t \approx 1645 \text{ cm}^{-1}, \end{aligned}$$

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 2E_g of the original cubic case would split into two orbital singlets ${}^2A_1(\theta)$ and ${}^2B_1(\epsilon)$, while the original lower orbital triplet ${}^2T_{2g}$ would be separated into an orbital singlet ${}^2B_2(\zeta)$ and a doublet ${}^2E(\eta, \xi)$ [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:

$$\begin{aligned} g_{//} &= g_e - 8 k' \zeta' / E_1 - 2k \zeta^2 / E_2^2 + 2 k' \zeta'^2 / E_1^2 \\ g_{\perp} &= g_e - 2k \zeta' / E_2 + 2 k' \zeta' \zeta [1/E_1 E_2 - 1/E_1^2] \end{aligned} \quad (8)$$

The energy denominators E_1 and E_2 stand for the energy separations between the excited ${}^2B_1, {}^2E$ and the ground 2B_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

$$\begin{aligned} E_1 &= 10D_q \\ E_2 &= -3D_s + 5D_t \end{aligned} \quad (9)$$

Applying the same parameters (D_s , D_t , D_q) (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 , κ (obtained by CDM) to Eq.(8) and then to Eq(7), the EPR parameters g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} 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 ($\approx 0.886 < 1$) in equation (3) and the moderate mixing coefficients (see Table 1) obtained from the cluster approach. Meanwhile, the ratio $(\zeta' + \zeta'')/2/\zeta_d$ (≈ 0.91) and the average $(k + k')/2$ (≈ 0.89) in the present work, approximately account for the covalency effect. This point may be illustrated by the comparable optical electronegativity (≈ 2.6) for V^{4+} with (≈ 3.2) for O^{2-} [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_{γ} and λ_{γ} (and λ_{σ}), spin-orbit coupling coefficients (in cm^{-1}) and the orbital reduction factors for VO^{2+} in Zn (antipyridine)₂(NO₃)₂

S_{dpt}	S_{dpc}	S_{ds}	A	N_{γ}	N_{σ}	λ_{γ}
0.05082	0.12968	0.10363	1.01018	0.9035	0.9555	0.3815
λ_{σ}	λ_{γ}	ζ	ζ'	k	k'	
0.3424	0.2736	234.0019	221.2665	0.9693	0.8195	

Table 2. The optical spectrum band positions (in cm^{-1}) and EPR parameters for VO^{2+} ions in Zn (antipyridine)₂(NO₃)₂

	Calculation			Expt ^[3]
	Cal ^a	Cal ^b	Cal ^c	
${}^2B_2 \rightarrow {}^2E$	--	17255	17133	17220/17270
	--		17372	
${}^2B_2 \rightarrow {}^2B_1$	--	21410	21422	21474/21283
${}^2B_2 \rightarrow {}^2A_1$	--	25225	25238	25212/25427
g_{\parallel}	1.9294	1.9344	1.9336	1.9336
g_{\perp}	1.9798	1.9761	1.9756	1.9761
A_{\parallel}	-167	-167	-167	171
A_{\perp}	-67	-67	-67	65.9

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

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

^cCalculations by using CDM in this work

(2) Many studies show that the core polarization κ in various V^{4+} (or VO^{2+}) clusters in crystals is in the range 0.6-1.0 [27, 28, 29]. The value $\kappa \approx 0.698$ 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 Sreeramachandra 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 $A_{\perp} \approx -65.9 \times 10^{-4} \text{cm}^{-1}$ [3]) 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 $[VO(H_2O)_5]^{2+}$ [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 (antipyridine)₂(NO₃)₂ and the theoretical EPR parameters based on the above contributions in this work are in good agreement with the experimental data.

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