Studies of the EPR *g*-Shift of $[Cr(CN)_6]^{3-}$ Clusters due to Crystal-Field and Charge-Transfer Mechanisms

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The EPR *g*-shift Δg ($\approx g - g_e$) of the metal-cyanide cluster $[Cr(CN)_6]^{3-}$ is calculated by high-order perturbation formulas based on both the crystal-field (CF) and charge-transfer (CT) mechanisms (the latter is often neglected in the crystal-field theory). The result agrees with the experimental value. The sign of the *g*-shift Δg_{CT} due to the contribution of the CT mechanism is opposite to that of Δg_{CF} due to the contribution of the CF mechanism, and the absolute value of Δg_{CT} is about 34% of that of Δg_{CF}. It appears that for transition metal ions in a strong covalent cluster, a reasonable theoretical explanation of the *g*-shift should take both the CF and CT mechanism into account.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-Field Theory; Charge-Transfer Mechanism; Cr^{3+}; $[Cr(CN)_6]^{3-}$.

1. Introduction

The EPR spectra of the metal-cyanide clusters $[Cr(CN)_6]^{3-}$ in crystals, such as alkali halides, have received interest [1 – 5]. It is found that within the cubic symmetry approximation, the *g*-factor of $[Cr(CN)_6]^{3-}$ clusters in various crystals is about 1.992(1) [1 – 5]. The small *g*-shift Δg ($\approx g - g_e$, where $g_e \approx 2.0023$ is the *g*-factor of the free electron) suggests that the covalence in $[Cr(CN)_6]^{3-}$ clusters is strong. In general, the contribution of covalence to the *g*-shift Δg comes from two effects: (i) The d electrons of the central $3d^n$ ion are mixed with the p electrons of ligands via the covalence effect, and so the spin-orbit (SO) coupling parameter of the ligand ion can contribute to the *g*-shift. In this case, a two-SO-parameter model (in which the contributions to the *g*-shift due to both the SO coupling parameter of the central $3d^n$ ion and that of ligands are included [6 – 8]) should be used. (ii) The strong covalence results in a lower charge-transfer (CT) energy level; thus the contribution to the *g*-shift Δg due to the mixture of the CT excited state with the ground state becomes larger, so that a reasonable explanation of the *g*-shift should take not only the crystal-field (CF) mechanism, but also the (CT) mechanism into account [9]. In $[Cr(CN)_6]^{3-}$ clusters, since the SO coupling parameter ζ_p^0 (≈ 49 cm^{-1} [10]) of the ligand ion C^{4-} is much smaller than that ($\zeta_d^0 \approx$ 273 cm^{-1} [11]) of the central ion Cr^{3+}, the second effect is more important. So, in this paper, we apply the complete high-order perturbation formula based on both mechanisms to calculate the *g*-shift Δg of $[Cr(CN)_6]^{3-}$ clusters in various crystals. The results (including the relative importance of the CT mechanism) are discussed.

2. Calculation

For an octahedral $3d^n$ MX_6 cluster, the one-electron basis functions based on the molecular orbital (MO) theory can be expressed as

$$|\Psi_\gamma\rangle = N_\gamma^X(|d_\gamma\rangle + \lambda_\gamma^X|p_\gamma\rangle), \tag{1}$$

where $|d_\gamma\rangle$ and $|p_\gamma\rangle$ are the d orbitals of the central $3d^n$ ion and p orbitals of ligands, respectively. The superscript X = a or b stands for anti-bonding orbitals (related to CF-excited states) or bonding orbitals (related to CT-excited states). The subscript γ = t or e indicates the irreducible representation t_{2g} or e_g of the

O_h group. N_γ^X and λ_γ^X denote the normalization coefficients and the orbital mixing coefficients, respectively.

From the above functions, and by adding the SO coupling Hamiltonian $H_{\mathrm{SO}}^{\mathrm{CT}}$ and the Zeeman term H_Z^{CT} based on the CT mechanism to the perturbation Hamiltonian in the CF mechanism, the complete high-order perturbation formula of the g-shift Δg including both the CF and CT mechanisms for the $3\mathrm{d}^3$ ions in the cubic octahedral cluster, was derived as [9]

$$\begin{aligned}
\Delta g &= \Delta g_{\mathrm{CF}} + \Delta g_{\mathrm{CT}},\\
\Delta g_{\mathrm{CF}} &= -\frac{8k'_{\mathrm{CF}}\zeta'_{\mathrm{CF}}}{3E_1} - \frac{4k'_{\mathrm{CF}}\zeta_{\mathrm{CF}}\zeta'_{\mathrm{CF}}}{9E_1^2} + \frac{2k_{\mathrm{CF}}\zeta'^2_{\mathrm{CF}}}{9E_1^2}\\
&\quad - \frac{4g_{\mathrm{s}}\zeta'^2_{\mathrm{CF}}}{9E_1^2} + \frac{4k_{\mathrm{CF}}\zeta'^2_{\mathrm{CF}}}{9E_3^2} - \frac{8g'_{\mathrm{s}}\zeta'^2_{\mathrm{CF}}}{9E_3^2}\\
&\quad - \frac{2k_{\mathrm{CF}}\zeta^2_{\mathrm{CF}}}{3E_2^2} - \frac{2g_{\mathrm{s}}\zeta^2_{\mathrm{CF}}}{3E_2^2} + \frac{4k'_{\mathrm{CF}}\zeta_{\mathrm{CF}}\zeta'_{\mathrm{CF}}}{9E_1E_3}\\
&\quad - \frac{4k'_{\mathrm{CF}}\zeta_{\mathrm{CF}}\zeta'_{\mathrm{CF}}}{3E_1E_2} + \frac{4k'_{\mathrm{CF}}\zeta_{\mathrm{CF}}\zeta'_{\mathrm{CF}}}{3E_2E_3},\\
\Delta g_{\mathrm{CT}} &= -\frac{8k'_{\mathrm{CT}}\zeta'_{\mathrm{CT}}}{3E_n},
\end{aligned} \tag{2}$$

in which the zero-order energy denominators E_i related to the CF mechanism are

$$\begin{aligned}
E_1 &= 10Dq, \quad E_2 = 15B + 5C,\\
E_3 &= 9B + 3C + 10Dq,
\end{aligned} \tag{3}$$

where Dq is the cubic field parameter and B and C are the Racah parameters. These parameters and the CT energy level E_n can be estimated from the optical spectra of the studied system. For $[\mathrm{Cr(CN)_6}]^{3-}$ clusters, from the optical spectra including the d-d transitions and charge-transfer from ligand to metal (CTLM) transition [12, 13] (all these transitions are shown in Table 1 of [12]), we have

$$\begin{aligned}
B &\approx 620\ \mathrm{cm^{-1}}, \quad C \approx 2985\ \mathrm{cm^{-1}},\\
Dq &\approx 2700\ \mathrm{cm^{-1}}, \quad E_n \approx 38\,600\ \mathrm{cm^{-1}}.
\end{aligned} \tag{4}$$

Since the one-electron basis functions include $\mathrm{t_{2g}}$ and $\mathrm{e_g}$ orbitals, the one-electron SO interaction involves two SO coupling parameters ζ and ζ'. The parameter ζ denotes the interaction only within $\mathrm{t_{2g}}$ orbitals, and ζ' the interaction between $\mathrm{t_{2g}}$ and $\mathrm{e_g}$ orbitals. The differentiation between ζ and ζ' is related to the covalence of the studied systems. Similar cases can also occur in the orbital reduction factor. Thus, in (2) we have two SO coupling parameters and orbital reduction factors related to the CF and CT mechanisms. From the crystal- and ligand-field theory they can be expressed as

$$\begin{aligned}
\zeta_{\mathrm{CF}} &= (N_{\mathrm{t}}^{\mathrm{a}})^2[\zeta_{\mathrm{d}}^0 + (\lambda_{\mathrm{t}}^{\mathrm{a}})^2\zeta_{\mathrm{p}}^0/2],\\
\zeta'_{\mathrm{CF}} &= N_{\mathrm{t}}^{\mathrm{a}} \cdot N_{\mathrm{e}}^{\mathrm{a}}[\zeta_{\mathrm{d}}^0 - \lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{e}}^{\mathrm{a}}\zeta_{\mathrm{p}}^0/2],\\
\zeta_{\mathrm{CT}} &= N_{\mathrm{t}}^{\mathrm{a}} \cdot N_{\mathrm{t}}^{\mathrm{b}}[\zeta_{\mathrm{d}}^0 + \lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{t}}^{\mathrm{b}}\zeta_{\mathrm{p}}^0/2],\\
\zeta'_{\mathrm{CT}} &= N_{\mathrm{t}}^{\mathrm{a}} \cdot N_{\mathrm{e}}^{\mathrm{b}}[\zeta_{\mathrm{d}}^0 - \lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{e}}^{\mathrm{b}}\zeta_{\mathrm{p}}^0/2],\\
k_{\mathrm{CF}} &= (N_{\mathrm{t}}^{\mathrm{a}})^2[1 - 2\lambda_{\mathrm{t}}^{\mathrm{a}}S_{\mathrm{dp}}(\mathrm{t_{2g}}) + (\lambda_{\mathrm{t}}^{\mathrm{a}})^2/2],\\
k'_{\mathrm{CF}} &= N_{\mathrm{t}}^{\mathrm{a}} \cdot N_{\mathrm{e}}^{\mathrm{a}}[1 + \lambda_{\mathrm{t}}^{\mathrm{a}}S_{\mathrm{dp}}(\mathrm{t_{2g}}) + \lambda_{\mathrm{e}}^{\mathrm{a}}S_{\mathrm{dp}}(\mathrm{e_g}) - \lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{e}}^{\mathrm{a}}/\sqrt{2}],\\
k_{\mathrm{CT}} &= N_{\mathrm{t}}^{\mathrm{a}} \cdot N_{\mathrm{t}}^{\mathrm{b}}[1 + (\lambda_{\mathrm{t}}^{\mathrm{a}} + \lambda_{\mathrm{t}}^{\mathrm{b}})S_{\mathrm{dp}}(\mathrm{t_{2g}}) + \lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{t}}^{\mathrm{b}}/2],\\
k'_{\mathrm{CT}} &= N_{\mathrm{t}}^{\mathrm{a}} \cdot N_{\mathrm{e}}^{\mathrm{b}}[1 + \lambda_{\mathrm{e}}^{\mathrm{b}}S_{\mathrm{dp}}(\mathrm{e_g}) + \lambda_{\pi}^{\mathrm{a}}S_{\mathrm{dp}}(\mathrm{t_{2g}}) - \lambda_{\mathrm{t}}^{\mathrm{a}}\lambda_{\mathrm{e}}^{\mathrm{b}}/2],
\end{aligned} \tag{5}$$

where ζ_{d}^0 and ζ_{p}^0 are the SO coupling parameters of the free $3\mathrm{d}^n$ ion and that of the free ligand ion. For the studied $[\mathrm{Cr(CN)_6}]^{3-}$ clusters, the values of ζ_{d}^0 and ζ_{p}^0 are given in the Introduction. $S_{\mathrm{dp}}(\gamma)$ is the group overlap integral. From the Slater-type self-consistent field (SCF) functions [14, 15] and the $\mathrm{Cr^{3+}}$-$\mathrm{C^{4-}}$ distance $R \approx 2.08$ Å in $[\mathrm{Cr(CN)_6}]^{3-}$ clusters [16], we obtain $S_{\mathrm{dp}}(\mathrm{t_{2g}}) \approx 0.05589$ and $S_{\mathrm{dp}}(\mathrm{e_g}) \approx 0.1154$.

Table 1. The molecular orbital coefficients in $[\mathrm{Cr(CN)_6}]^{3-}$ clusters.

$N_{\mathrm{e}}^{\mathrm{a}}$	$N_{\mathrm{t}}^{\mathrm{a}}$	$\lambda_{\mathrm{e}}^{\mathrm{b}}$	$\lambda_{\mathrm{t}}^{\mathrm{b}}$	$N_{\mathrm{e}}^{\mathrm{b}}$	$N_{\mathrm{t}}^{\mathrm{b}}$
0.9376	0.9138	2.4251	2.1697	0.3994	0.4099

Table 2. The spin-orbit coupling parameters (in $\mathrm{cm^{-1}}$) and orbital reduction factors related to the CF and CT mechanisms in $[\mathrm{Cr(CN)_6}]^{3-}$ clusters.

ζ_{CF}	ζ'_{CF}	ζ_{CT}	ζ'_{CT}	k_{CF}	k'_{CF}	k_{CT}	k'_{CT}
233.2	228.6	92.2	110.6	0.8940	0.6741	0.2048	0.6799

Table 3. The g-shift Δg ($\approx g - g_{\mathrm{e}}$) of $[\mathrm{Cr(CN)_6}]^{3-}$ clusters.

Δg_{CF}	Δg_{CT}	Δg(total)	Δg (Expt. [1 – 5])
−0.0155	0.0052	−0.0103	−0.0103(10)

From the one-electron basis functions in (1), the MO coefficients N_γ^X and λ_γ^X can be related by the normalization relationships

$$N_\gamma^X[1 + 2\lambda_\gamma^X S_{\mathrm{dp}}(\gamma) + (\lambda_\gamma^X)^2]^{1/2} = 1 \tag{6}$$

and the orthonormal relations

$$\lambda_\gamma^{\mathrm{b}} = -\frac{1 + \lambda_\gamma^{\mathrm{a}} S_{\mathrm{dp}}(\gamma)}{\lambda_\gamma^{\mathrm{a}} + S_{\mathrm{dp}}(\gamma)}. \tag{7}$$

Thus, in the above formulas, if the MO coefficients $\lambda_\gamma^{\mathrm{a}}$ are known, the other MO coefficients N_γ^{a}, $\lambda_\gamma^{\mathrm{b}}$ and

N_γ^{b}, the parameters in (5) and hence the g-shift Δg can be calculated. We take $\lambda_\gamma^{\mathrm{a}}$ ($= \lambda_{\mathrm{t}}^{\mathrm{a}} = \lambda_{\mathrm{e}}^{\mathrm{a}}$ for decreasing the number of adjustable parameters) as the only adjustable parameter. By fitting the calculated g-shift Δg of $[Cr(CN)_6]^{3-}$ to the experimental value, we obtain

$$\lambda_\gamma^{\mathrm{a}} \approx -0.5038. \qquad (8)$$

The other MO coefficients and the parameters in (5) are, respectively, shown in Tables 1 and 2. The comparison between the calculated and experimental g-shift Δg is shown in Table 3.

3. Discussion

Table 2 shows that the parameter ζ and factor k are indeed different from the corresponding parameter ζ' and factor k', suggesting that the studied $[Cr(CN)_6]^{3-}$ clusters have strong covalence.

Table 3 shows that, if only the CF mechanism is considered, the calculated g-shift Δg_{CF} of $[Cr(CN)_6]^{3-}$ clusters agrees poorly with the observed value, whereas, if the contribution Δg_{CT} of the CT mechanism is added, the calculated $\Delta g(\text{total})$ is consistent with the observed value. The contribution Δg_{CT} due to the CT mechanism is opposite in sign and about 34% in magnitude compared with the contribution Δg_{CF} due to the CF mechanism. So, for $[Cr(CN)_6]^{3-}$ and other transition metal cyanide clusters $[M(CN)_6]^{n-}$, because of the strong covalence, a reasonable theoretical explanation of the g-shift (or other EPR parameters) should take both the CF and CT mechanism into account.

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