

Magnetic Properties of a Low Symmetry d^5 Complex: An Adiabatic Pseudo-Jahn–Teller Problem

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This chapter is dedicated to Professor Isaak Bersuker on the occasion of his 75th birthday – as a sign of our appreciation of his outstanding contribution to the theory of the Jahn–Teller effect

Abstract

A vibronic model for the magnetic properties of a low-spin d^5 metal complex is reported. The splitting of the ground 2T_2 -term by the strong spin–orbital interaction and the trigonal component of the crystal field as well as the covalency effects are taken into account. The pseudo-Jahn–Teller mixing of the low-lying states is also considered in the framework of the semiclassical adiabatic approximation. The influence of the named interactions on the g -tensor and on the tensor of the temperature-independent paramagnetism is elucidated.

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1. INTRODUCTION

Complexes of heavy metal ions attract considerable interest due to the strong spin–orbital interaction giving rise to a significant magnetic anisotropy. This study was initiated by the unusual magnetic data obtained at Texas A&M University for two compounds of Re(II): $[\text{Et}_4\text{N}][\text{Re}(\text{triphos})(\text{CN}_3)]$ and $[\text{Re}(\text{triphos})(\text{MeCN}_3)] [\text{BF}_4]_2$ in which Re(II) ions occupy the sites with a strong cubic crystal field and a significant trigonal component. These complexes exhibit anomalously large temperature-independent paramagnetism (TIP) that can be related to the low-lying levels that arise from the interplay between the low-symmetry crystal field, spin–orbital and vibronic interactions. Since the cubic crystal field for the heavy metal ions is usually strong the d^5 electronic configuration is expected to be the low-spin ground term ${}^2T_2(t_2^5)$ that is split by spin–orbital interaction and trigonal crystal field. The studies of the orbital triplets in the crystal field were focused mainly on the calculation of the EPR parameters [1–4]. In the present study we will use the T–P isomorphism [2] and pay attention to the magnetic properties of the d^5 complexes. The vibronic Jahn–Teller (JT) interaction is of crucial importance for the interpretation of the magnetic and spectroscopic properties of transition metal complexes [5–7]. A special role of the JT interaction in the magnetic problem has been demonstrated in [8], where the giant second-order Zeeman effect has been discovered. This effect was shown to arise from the set of closely spaced hybrid electron-vibrational levels. The JT interaction for the extended 5d electronic shells is expected to be strong and should be taken into account along with the spin–orbital interaction. For the case under study (d^5 -ion) this leads to a pseudo-JT (PJT) vibronic problem. Using semiclassical adiabatic approach [9] we elucidate the main manifestations of the PJT interaction and the combined action of PJT and trigonal crystal field in the magnetic properties of complex d^5 ions.

2. THE MODEL

We consider d^5 -ions in the cubic and axially distorted complexes. Axial distortions are assumed to arise from the heteronuclear ligand surrounding or from deviation of the local surrounding of the metal ion from the octahedral one. This gives rise to a trigonal or a tetragonal component of the crystal field. The model takes into account the following relevant interactions defining the magnetic properties of the complexes: (1) Strong cubic crystal field. In a strong cubic crystal field the d^5 -ion proves to be the low-spin one and has a triplet ground state ${}^2T_2(t_2^5)$; (2) spin–orbital coupling that splits the 2T_2 -term into the doublet Γ_7 and the quadruplet Γ_8 ; (3) trigonal component of the crystal field which is compatible with the structure of the titled Re(II) complexes; (4) vibronic coupling in the orbital triplet with the tetragonal (e) modes that leads to a PJT vibronic problem $T_2 \otimes (e + \text{SO})$ in d^5 complexes. Here we will consider the combined effect of the low-symmetry fields and PJT interaction with the tetragonal vibrations that usually is the most important.

We shall employ the adiabatic approximation that was shown to provide a rather good accuracy in the calculation of the magnetic susceptibility for the vibronic mixed valence systems exhibiting PJT in a wide range of parameters [9]. At the same time this approximation allows us to gain a descriptive comprehension of the physical role of the JT interaction. The full Hamiltonian of the system in the adiabatic approximation can be written as follows:

$$\mathbf{H} = \mathbf{H}_{\text{SO}} + \mathbf{V}_{\text{trig}} + \mathbf{H}_{\text{Z}} + \frac{1}{2} \omega_E (q_u^2 + q_v^2) \mathbf{I} + v_E (q_u \mathbf{O}_u + q_v \mathbf{O}_v) \quad (1)$$

The Hamiltonian of the electronic subsystem includes the spin–orbital coupling (\mathbf{H}_{SO}), trigonal crystal field (\mathbf{V}_{trig}) and Zeeman interaction (\mathbf{H}_{Z}). The vibronic part of the Hamiltonian contains the energy of free vibrations associated with the tetragonal (e) JT modes and the vibronic coupling with these modes, v_E is the vibronic constant. The dimensionless normal coordinates of the tetragonal vibrations are denoted as q_u, q_v (basis $u \propto 3z^2 - r^2, v \propto x^2 - y^2$) and ω_E is the frequency of these vibrations. In equation (1), \mathbf{I} is the unit matrix and the matrices $\mathbf{O}_{E\gamma} \equiv \mathbf{O}_\gamma$ ($\gamma = u, v$) are defined in the cubic T_2 -basis (ξ, η, ζ) as follows:

$$\mathbf{O}_{Eu} = \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{O}_{Ev} = \begin{pmatrix} \sqrt{3}/2 & 0 & 0 \\ 0 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2)$$

In the framework of the adopted semiclassical adiabatic approximation the nuclear kinetic energy is omitted.

3. MATRIX REPRESENTATION OF THE MAIN INTERACTIONS

We shall use the T – P -isomorphism that allows us to consider the orbital triplet T_2 as a state possessing the fictitious orbital angular momentum $\mathbf{L} = 1$, keeping in mind that the matrix elements of the angular momentum operator \mathbf{L} within T_2 and P bases are of the opposite signs, $\mathbf{L}(T_2) = -\mathbf{L}(P)$ [2]. As it was shown in our recent paper [10] this approach provides both an efficient computational tool and a clear insight on the magnetic anisotropy of the system that appears due to the orbital contributions. Within T – P formalism the spin–orbital and Zeeman terms can be represented as:

$$\mathbf{H}_{\text{SO}} = -\kappa \lambda \mathbf{L} \mathbf{S}, \quad \mathbf{H}_{\text{Z}} = \beta (g_e \mathbf{S} - \kappa \mathbf{L}) \mathbf{H} \quad (3)$$

The operators in equation (3) act within the ground manifold possessing $S = \frac{1}{2}$ and $\mathbf{L} = 1$ (κ is the orbital reduction factor, g_e is the electronic g -factor). The axial (trigonal) component of the crystal field directed along the C_3 -axis is defined as a linear combination of the irreducible tensors of O_h that becomes scalar in the

trigonal point groups let say, (D_{3d}):

$$\mathbf{V}_{\text{trig}} = -\frac{1}{2}\Delta(\mathbf{O}_{\xi} + \mathbf{O}_{\eta} + \mathbf{O}_{\zeta}) \quad (4)$$

where the matrices $\mathbf{O}_{T_2\gamma} \equiv \mathbf{O}_{\gamma}$ ($\gamma = \xi, \eta, \zeta$) are given by:

$$\mathbf{O}_{T_2\xi} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \mathbf{O}_{T_2\eta} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \mathbf{O}_{T_2\zeta} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (5)$$

In equation (4) Δ is the parameter of the trigonal crystal field. This crystal field splits the T_2 -state into an orbital singlet and a doublet, the parameter Δ is defined in such a way that for positive Δ the ground state is the orbital singlet.

To take advantage from the pseudo-angular momentum representation we shall employ the technique of the irreducible tensor operators as suggested in Ref. [10]. One can easily establish the following interrelations between the matrices $\mathbf{O}_{\Gamma\gamma}$ and the orbital angular momentum operators:

$$\begin{aligned} \mathbf{O}_{Eu} &= 1 - \frac{3}{2}\mathbf{L}_Z^2, & \mathbf{O}_{Ev} &= -\frac{\sqrt{3}}{2}(\mathbf{L}_X^2 - \mathbf{L}_Y^2) \\ \mathbf{O}_{T_2\xi} &= -\frac{1}{\sqrt{2}}(\mathbf{L}_Y\mathbf{L}_Z + \mathbf{L}_Z\mathbf{L}_Y), & \mathbf{O}_{T_2\eta} &= -\frac{1}{\sqrt{2}}(\mathbf{L}_X\mathbf{L}_Z + \mathbf{L}_Z\mathbf{L}_X) \\ \mathbf{O}_{T_2\zeta} &= -\frac{1}{\sqrt{2}}(\mathbf{L}_X\mathbf{L}_Y + \mathbf{L}_Y\mathbf{L}_X) \end{aligned} \quad (6)$$

Let us express the operators \mathbf{L}_X , \mathbf{L}_Y and \mathbf{L}_Z in terms of the components of the first rank spherical irreducible tensor \mathbf{L}_{1q} ($q = 0, \pm 1$):

$$\mathbf{L}_X = \frac{1}{\sqrt{2}}(\mathbf{L}_{1-1} - \mathbf{L}_{11}), \quad \mathbf{L}_Y = \frac{i}{\sqrt{2}}(\mathbf{L}_{1-1} + \mathbf{L}_{11}), \quad \mathbf{L}_Z = \mathbf{L}_{10} \quad (7)$$

The same relations can be applied to the spin operators. Then, using the Clebsch–Gordan decomposition [11] one can express the bilinear forms of the orbital angular momentum operators in equation (6) in terms of the irreducible tensorial products:

$$\mathbf{L}_{1q_1}\mathbf{L}_{1q_2} = \sum_{kq} \{\mathbf{L}_1 \otimes \mathbf{L}_1\}_{kq} C_{1q_1 1q_2}^{kq} \quad (8)$$

Here $\{\mathbf{L}_1 \otimes \mathbf{L}_1\}_{kq}$ is the complex irreducible tensor of the rank k composed from the angular momentum operators, $q = -k, -k+1, \dots, k$ and $C_{1q_1 1q_2}^{kq}$ are the Clebsch–Gordan (Wigner) coefficients. Now one can express all matrices $\mathbf{O}_{\Gamma\gamma}$ in terms of the complex irreducible tensors $\mathbf{T}_{kq}(\mathbf{L}) = \{\mathbf{L}_1 \otimes \mathbf{L}_1\}_{kq}$ acting in the orbital subspace:

$$\begin{aligned}
\mathbf{O}_{Eu} &= -\sqrt{\frac{3}{2}}\mathbf{T}_{20}(\mathbf{L}), & \mathbf{O}_{Ev} &= -\sqrt{\frac{3}{2}}[\mathbf{T}_{22}(\mathbf{L}) + \mathbf{T}_{2-2}(\mathbf{L})] \\
\mathbf{O}_{T_2\xi} &= -\frac{i}{\sqrt{2}}[\mathbf{T}_{21}(\mathbf{L}) + \mathbf{T}_{2-1}(\mathbf{L})], & \mathbf{O}_{T_2\eta} &= \frac{1}{\sqrt{2}}[\mathbf{T}_{21}(\mathbf{L}) - \mathbf{T}_{2-1}(\mathbf{L})] \\
\mathbf{O}_{T_2\zeta} &= \frac{i}{\sqrt{2}}[\mathbf{T}_{22}(\mathbf{L}) - \mathbf{T}_{2-2}(\mathbf{L})]
\end{aligned} \quad (9)$$

These relations allow us to evaluate the matrix elements of all involved interactions using the irreducible tensor operator technique and to exploit the results derived from the theory of magnetically coupled systems. The matrix of the Hamiltonian can be built either in uncoupled or in coupled bases. It is convenient to choose such a basis in which spin–orbital coupling proves to be diagonal. This means that in this basis the orbital angular momentum and spin are coupled $|LSJM_J\rangle \equiv |1\frac{1}{2}JM_J\rangle$ in order to get the total angular momentum $J = \frac{1}{2}$ (Kramers doublet Γ_7) and $J = \frac{3}{2}$ (quadruplet Γ_8). The quantization axis for the total angular momentum in the trigonally distorted system is C_3 . In the coupled basis the spin–orbital operator is represented by the diagonal matrix:

$$\langle 1S'J'M'_J | \mathbf{H}_{SO} | 1SJM_J \rangle = -\frac{1}{2}\kappa\lambda[J(J+1) - S(S+1) - 2]\delta_{J'J'}\delta_{M_JM'_J} \quad (10)$$

Then, using the matrix elements for the complex irreducible tensor operators (see Ref. [11]) we arrive at the following expression for the matrix elements of the vibronic interaction:

$$\begin{aligned}
&\langle 1S'J'M'_J | \mathbf{H}_{\text{vib}} | 1SJM_J \rangle \\
&= (-1)^{S+J}\sqrt{5(2J+1)} \begin{Bmatrix} 1 & 2 & 1 \\ J' & S & J \end{Bmatrix} v_E \frac{\sqrt{3}}{2} [q_u \sqrt{2} C_{JM_J20}^{J'M'_J} \\
&\quad + q_v (C_{JM_J22}^{J'M'_J} + C_{JM_J2-2}^{J'M'_J})]
\end{aligned} \quad (11)$$

where $\{\dots\}$ are the $6j$ -symbols [11]. For the matrix elements of Zeeman interaction one gets:

$$\begin{aligned}
&\langle 1S'J'M'_J | \mathbf{H}_Z | 1SJM_J \rangle \\
&= \sqrt{(2J+1)}(-1)^{J+S} \begin{Bmatrix} 1 & 1 & 1 \\ J' & S & J \end{Bmatrix} \beta [g_e \sqrt{S(S+1)(2S+1)} + \kappa\sqrt{6}] (C_{JM_J10}^{J'M'_J} H_{10} \\
&\quad - C_{JM_J11}^{J'M'_J} H_{1-1} - C_{JM_J1-1}^{J'M'_J} H_{11})
\end{aligned} \quad (12)$$

where $H_{10} = H_Z$, $H_{1\pm 1} = \mp(1/\sqrt{2})(H_X \pm iH_Y)$ are the cyclic components of the magnetic field. Particular direction of the magnetic field can be selected by means of an appropriate choice of the corresponding terms in equation (12).

Finally, for the matrix elements of the trigonal crystal field operators we find:

$$\begin{aligned} & \langle 1 S J' M'_J | \mathbf{V}_{\text{trig}} | 1 S J M_J \rangle \\ &= (-1)^{1+S+J} \sqrt{5(2J+1)} \begin{Bmatrix} 1 & 2 & 1 \\ J' & S & J \end{Bmatrix} \frac{1}{2\sqrt{2}} \Delta [(i-1)C_{J M_J 2 1}^{J' M'_J} \\ &+ (i+1)C_{J M_J 2 -1}^{J' M'_J} - i(C_{J M_J 2 2}^{J' M'_J} - C_{J M_J 2 -2}^{J' M'_J})] \end{aligned} \quad (13)$$

In the following sections we will consider the interplay of the vibronic interaction, spin-orbital coupling and static trigonal field with regard to the problem of the magnetic properties of the low-symmetry d^5 -complexes.

4. ENERGY PATTERN FOR A d^5 COMPLEX IN A STATIC MODEL

Before studying the magnetic properties in the vibronic model we will inspect the arrangement of the energy levels taking into account only electronic interactions: spin-orbital coupling and trigonal crystal field. The spin-orbital coupling parameter is negative for the low-spin d^5 -ions, so that in the cubic crystal field the Kramers doublet Γ_7 is the ground state and the quadruplet Γ_8 is the excited one. The corresponding energies are the following:

$$E\left(\frac{1}{2}\right) = -\kappa|\lambda|, \quad E\left(\frac{3}{2}\right) = \frac{\kappa|\lambda|}{2} \quad (14)$$

The energy separation between the doublet and quadruplet is $3\kappa|\lambda|/2$. When the system is distorted along the C_3 axis the O_h symmetry is lowered to D_{3d} . Then the irreducible representation Γ_7 passes to Γ_4 while Γ_8 splits into $\Gamma_4 + \Gamma_5 + \Gamma_6$ [12]. The representations Γ_5 and Γ_6 form the complex conjugated double-valued representation with the basis $M_J = \pm 3/2$, while the basis for Γ_4 is $M_J = \pm 1/2$. Two Γ_4 states (from $J = 1/2$ and $3/2$) with the same quantum number M_J are mixed by the trigonal crystal field. In the absence of external magnetic field the energy levels are solely determined by $|M_J|$ due to the axial symmetry of the system. The expressions for the energy levels $E(|M_J|)$ are found to be the following:

$$E_{\pm}\left(\frac{1}{2}\right) = \frac{1}{4} \left[-\Delta - |\lambda|\kappa \pm \sqrt{(\Delta - 3|\lambda|\kappa)^2 + 8\Delta^2} \right], \quad E\left(\frac{3}{2}\right) = \frac{\Delta}{2} + \frac{|\lambda|\kappa}{2} \quad (15)$$

Hereunder we use the notations $E_{\pm}(\frac{1}{2})$ for the energies of the Γ_4 -states and $E(\frac{3}{2})$ for the energy of the $\Gamma_5 + \Gamma_6$ -state. The corresponding wave-functions depend on the sign of the trigonal crystal field. So, provided $\Delta \leq 0$, the wave-functions of the ground Γ_4 -state are the following:

$$\Psi_{-}\left(\pm\frac{1}{2}\right) = \sqrt{\frac{1+R}{2}} \Phi\left(\frac{1}{2}, \pm\frac{1}{2}\right) \pm \sqrt{\frac{1-R}{2}} \Phi\left(\frac{3}{2}, \pm\frac{1}{2}\right) \quad (16)$$

where:

$$R = \left[1 + 8 \left(1 - 3 \frac{|\lambda|\kappa}{\Delta} \right)^{-2} \right]^{-1/2} \quad (17)$$

Figure 1 shows the energy levels of the d^5 system as a function of Δ providing $\lambda = -2100 \text{ cm}^{-1}$ and $\kappa = 0.7$. Independently of the sign and magnitude of the trigonal crystal field the doublet Γ_4 with the energy $E_-(\frac{1}{2})$ is the ground state. In the limit of strong positive trigonal field the spin–orbital coupling is completely suppressed within the ground state, so this state becomes 2A_1 . The symmetry of the first excited state depends on the sign of the trigonal field. Providing $\Delta < 0$ the first excited level is $E(\frac{3}{2})$. In the limit of strong negative field two low-lying levels $E_-(\frac{1}{2}), E(\frac{3}{2})$ vs. trigonal field are parallel, these levels can be attributed to the first order spin–orbital splitting of the trigonal 2E term in D_{3d} symmetry. Only the L_Z component is operative within the orbital trigonal E -basis, so that spin–orbital coupling becomes axial ($-\kappa\lambda L_Z S_Z$) and one easily finds that the spin–orbital splitting in 2E is $\kappa\lambda$. This value is reduced by the trigonal crystal field with respect to its initial value ($3\kappa\lambda/2$) in a cubic 2T_2 term. Using equations (16) and (17) one can find the following formulas for the g -factors that are valid in the case of a negative trigonal field:

$$g_{\parallel} = 1 + R + 2\sqrt{2(1 - R^2)}, \quad g_{\perp} = 1 + R - \sqrt{2(1 - R^2)} \quad (18)$$

In the limit of strong negative trigonal field the parameter R takes on the value $\frac{1}{3}$, we approach the following principal values of g -factor: $g_{\parallel} = 4$ and $g_{\perp} = 0$. This case can be referred to as the fully anisotropic limit.

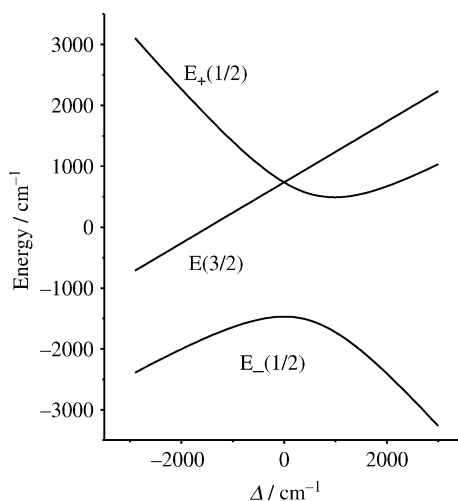


Fig. 1. Splitting of the ${}^2T_2(t_2^5)$ term by the spin–orbital interaction and trigonal crystal field.

When $\Delta > 0$ the first excited level is $E_+(\frac{1}{2})$. Now the above discussed first-order spin-orbital splitting of 2E -term occurs for the excited levels $E(\frac{3}{2})$, $E_+(\frac{1}{2})$ that are parallel in the strong crystal field limit.

5. g -FACTORS AND TIP IN THE ${}^2T_2 \otimes (e + \text{SO} + \mathbf{V}_{\text{trig}})$ PSEUDO-JT VIBRONIC PROBLEM

The tetragonal vibrational modes couple the states $E_-(\frac{1}{2})$ and $E_+(\frac{1}{2})$ (Fig. 1) that results in the PJT problem. In order to make clear the behavior of the g -factors and TIP contributions to the magnetic susceptibility we start with the inspection of the adiabatic surfaces. Figure 2(a) illustrates the ground adiabatic potential sheet of a perfect octahedral system ($\Delta = 0$) in the case of weak vibronic coupling when this interaction is not strong enough to produce the tetragonal minima. Then the only minimum corresponds to a non-distorted octahedron ($q_u = q_v = 0$). With the increase of the vibronic coupling the adiabatic well in the vicinity of the minimum is getting more flat and for some critical value of the vibronic constant this single-minimum is split into three equivalent minima located at the positions $(q_u, q_v) = (-q_0, 0)$, $(q_0/2, -q_0\sqrt{3}/2)$, $(q_0/2, q_0\sqrt{3}/2)$ lying on the ring with the radius q_0 , q_0 being a function of all relevant parameters of the system. In each minimum the system is distorted along one of three tetragonal axes. With further increase of the vibronic coupling these minima become deeper (Fig. 2(b)).

The trigonal field and vibronic coupling with the tetragonal modes are in competition and the field modulates the energy separation between the $E_-(\frac{1}{2})$ and $E_+(\frac{1}{2})$ states governing thus the strength of the PJT effect. With the increase of the trigonal field, the minima of the lower adiabatic surface become shallower, the barrier separating the minima decreases (Fig. 2(c)) and at some critical value of the field (Fig. 2(d)) they are transformed into one minimum. This tendency remains irrespectively of the sign of the static distortion. Note, however, that for $\Delta > 0$ the shape of the adiabatic surface changes non-monotonically. In fact, with the increase of Δ , firstly, the two low-lying doublets become closer and then diverge (Fig. 1).

Positions of the minima in (q_u, q_v) space are related to the tetragonal distortions of the system. At the same time this space does not contain points corresponding to the additional trigonal distortions related to the trigonal field. The real distortions of the system in each minimum of the adiabatic potential can be presented as a superposition of the tetragonal distortion produced by the JT interaction and the trigonal distortion arising from the static crystal field; the last can be described in the extended vibrational space involving also trigonal (t_2) vibrations as a shift of the trigonal coordinate $Q = (q_\xi + q_\eta + q_\zeta)/\sqrt{3}$. In order to find the real symmetry of the system (that should be implied in the description of g -tensors and tensors of the TIP) one can construct the effective crystal field potential arising from the combined tetragonal (JT type) and trigonal (static) distortions, i.e., shift of Q . Crystal field potentials corresponding to the tetragonal distortions along C_4 axes X , Y and Z can be

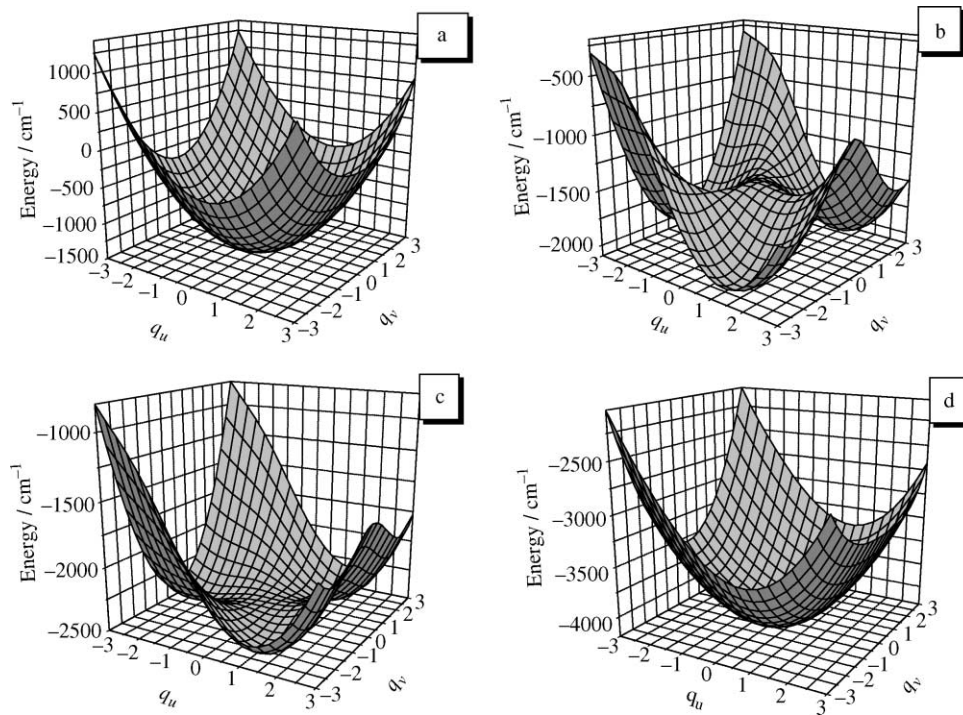


Fig. 2. The lower sheet of the adiabatic potential: $\lambda = -2100 \text{ cm}^{-1}$, $\kappa = 0.7$, $\hbar\omega = 400 \text{ cm}^{-1}$ and (a) $\nu = 1.5 \hbar\omega$, $\Delta = 0$, (b) $\nu = 3 \hbar\omega$, $\Delta = 0$, (c) $\nu = 3 \hbar\omega$, $\Delta = 2000 \text{ cm}^{-1}$, (d) $\nu = 3 \hbar\omega$, $\Delta = 4000 \text{ cm}^{-1}$.

associated with three non-orthogonal combinations of the E_g -type:

$$V_Z = V_{Eu}, \quad V_Y = -\frac{1}{2}V_{Eu} - \frac{\sqrt{3}}{2}V_{Ev}, \quad V_X = -\frac{1}{2}V_{Eu} + \frac{\sqrt{3}}{2}V_{Ev} \quad (19)$$

The trigonal distortion with C_3 axis [111] is related to the operator of T_2 -type:

$$(V_{T_2\xi} + V_{T_2\eta} + V_{T_2\zeta}/\sqrt{3}) \quad (20)$$

By substituting the coordinate representation for the operators involved in equations (19) and (20) one can find three crystal field operators corresponding to three tetragonal minima in the trigonally distorted system:

$$\begin{aligned} W_Z &= A(3z^2 - r^2) + B(yz + xz + xy) \\ W_Y &= A(3y^2 - r^2) + B(yz + xz + xy) \\ W_X &= A(3x^2 - r^2) + B(yz + xz + xy) \end{aligned} \quad (21)$$

Inspecting these potentials one can easily see that in each tetragonal minimum the system really belongs to the C_s point group (that is, in fact, the intersection of D_{4h} and D_{3d}) with the symmetry planes σ_{XY} , σ_{ZY} and σ_{XZ} , respectively. The parameters A and B are defined by competition of the PJT interaction and trigonal field, in particular, when the trigonal field suppresses tetragonal distortions and the potential becomes single-minimum, the parameter A vanishes. In this case the system proves to be trigonal.

The g and TIP tensors under the actual symmetry prove to be tri-axial. The main axes of g and TIP in each minimum are located in the corresponding planes σ and the directions of these axes cannot be determined by symmetry arguments solely, they move from C_4 (limit of strong PJT) to C_3 (strong trigonal field). When the tunneling processes are fast enough the observable g -factors are to be averaged over tetragonal minima that correspond to an average potential in equation (21). Summation over C_4 directions (over three minima) leaves only trigonal component, so that we arrive to the axial g -factors with the main axis C_3 . For the static susceptibility experiment the time scale is practically infinite, so the TIP tensor can be always regarded to C_3 axis.

To illustrate the behavior of g -factors in a simple way we assume that the tunneling is fast so that we are dealing with the averaged, i.e., trigonal symmetry. In this case for a three-well surface one can obtain the approximate expressions for the main components of g -factors and TIP:

$$\begin{aligned} g_{\parallel} &= \left(\frac{1}{3} \sum_{i=1}^3 g_{\bar{Z}\bar{Z}}^2(q_u^i, q_v^i) \right)^{1/2}, & g_{\perp} &= \left(\frac{1}{3} \sum_{i=1}^3 g_{\bar{X}\bar{X}}^2(q_u^i, q_v^i) \right)^{1/2} \\ \text{TIP}_{\parallel} &= \frac{1}{3} \sum_{i=1}^3 \text{TIP}_{\bar{Z}\bar{Z}}(q_u^i, q_v^i), & \text{TIP}_{\perp} &= \frac{1}{3} \sum_{i=1}^3 \text{TIP}_{\bar{X}\bar{X}}(q_u^i, q_v^i) \end{aligned} \quad (22)$$

where \bar{X} , \bar{Y} and \bar{Z} are the trigonal axes, \bar{Z} coincides with the C_3 axis, q_u^i and q_v^i are the

coordinates of the i th minimum ($i = 1, 2, 3$). In the case of one minimum the g -factors and TIP are simply defined in the point $q_u = q_v = 0$, in this case the electronic wave-function can be associated with the function of a trigonal singlet, $(\xi + \eta + \zeta)/\sqrt{3}$.

In order to simplify the understanding of the magnetic behavior of the PJT system first we give some results for the limiting cases of strong crystal field ($|\Delta| \gg \nu$) when the PJT effect is completely quenched. Depending on the sign of Δ we face two cases. For $\Delta > 0$ the ground orbital singlet is well separated from excited ones so the spin–orbital coupling is suppressed. The system becomes isotropic and the g -factor takes on the spin-only value. Provided that $\Delta < 0$ the spin–orbital interaction is partially reduced. In this case we arrive at the fully anisotropic limit with $g_{\parallel} = 4$ and $g_{\perp} = 0$. Finally, when $\Delta = 0$ we obtain the isotropic g -factor that is different from the spin-only value due to the effect of covalence. In our case ($\kappa = 0.7$) g is equal to 1.6.

Figure 3 shows the averaged g_{\parallel} and g_{\perp} values as functions of the vibronic coupling parameter for $\Delta < 0$. When the vibronic coupling is weak, the g vs. $\nu/\hbar\omega$ curves exhibit plateaus. These plateaus appear due to the fact that for small vibronic coupling the lower sheet of the adiabatic surface has the only minimum. In this case g_{\parallel} and g_{\perp} values are just the same as those calculated within the static model. The increase of the absolute value of Δ tends to increase the anisotropy (g_{\parallel} goes up and g_{\perp} goes down). In the limiting case of very strong field the anisotropy reaches its

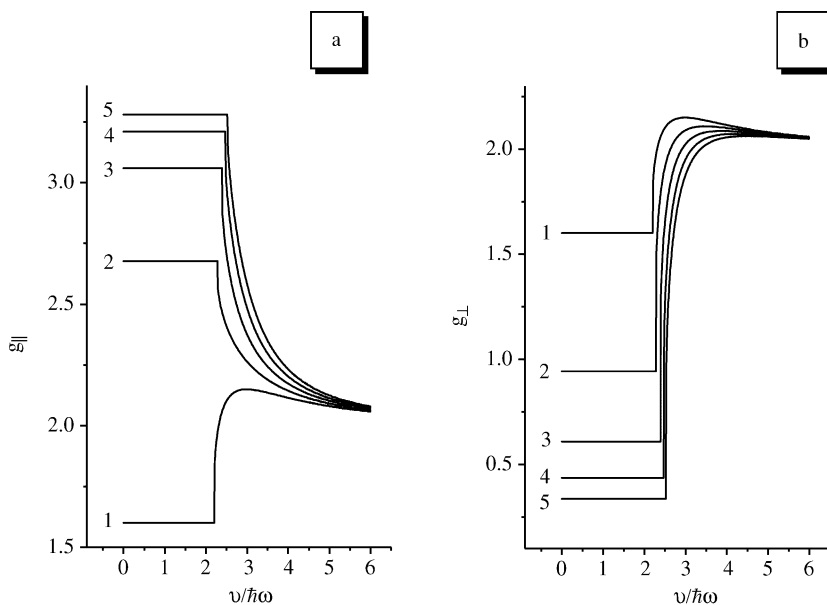


Fig. 3. Calculated principal values of the g -factors as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = -1000 \text{ cm}^{-1}$, (3) $\Delta = -2000 \text{ cm}^{-1}$, (4) $\Delta = -3000 \text{ cm}^{-1}$, (5) $\Delta = -4000 \text{ cm}^{-1}$.

maximum ($g_{\parallel} = 4$ and $g_{\perp} = 0$). Each plateau ends at some critical value $\nu = \nu_C$ corresponding to the condition of instability for which a single-minimum surface is transformed into the surface possessing three quasi-tetragonal minima (Fig. 2). In this case both components of g -factor start to change in such a way that the anisotropy decreases. In the limit of strong vibronic coupling the anisotropy of g -factor disappears and g -factor reaches its pure spin value.

The case $\Delta > 0$ is presented in Fig. 4. The behavior of the g -factors is similar to that in the previous case but two differences should be noted. With the increase of trigonal field the difference between g_{\parallel} and g_{\perp} (i.e., the anisotropy of the g -factor) increases, passes through the maximum and then decreases. In the strong crystal field limit the g -factor becomes isotropic with $g_{\parallel} = g_{\perp} = g_e$. For relatively small positive Δ the non-monotonic dependence of the g -factors vs. $\nu/\hbar\omega$ is connected with the behavior of the energy levels in this range (see discussion in Section 4). Irrespective of the sign of the crystal field the strong vibronic coupling stabilizes the ground singlet state and consequently suppresses the spin–orbital interaction.

The TIP contributions as functions of $\nu/\hbar\omega$ are shown in Figs 5 and 6. The main common feature of TIP_{\parallel} and TIP_{\perp} is the presence of the plateau for relatively small values of vibronic parameter. However, for $\Delta < 0$ contrary to the g -factors the TIP_{\parallel} values decrease with the growth of $|\Delta|$. In the limit of strong fields TIP_{\parallel} vanishes. At the same time in the range of small ν -values TIP_{\perp} remains practically constant. Thus TIP demonstrates a strong anisotropy just like the g -factors. This anisotropy comes

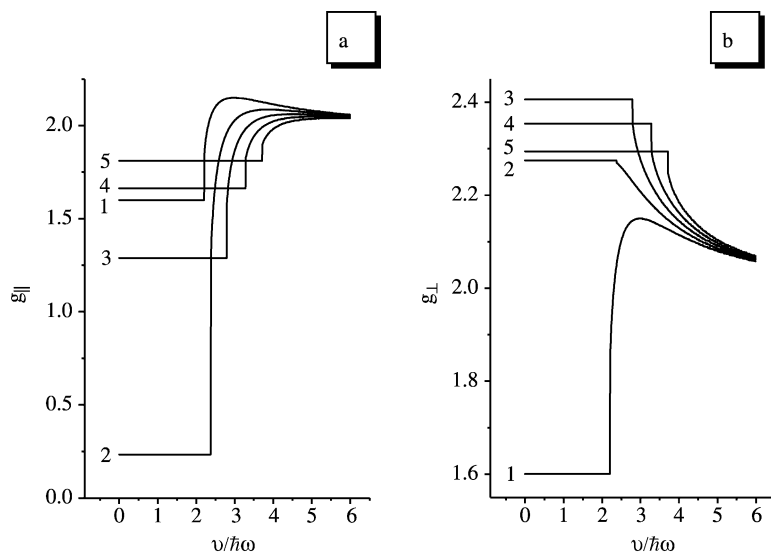


Fig. 4. Calculated principal values of the g -factors as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = 1000 \text{ cm}^{-1}$, (3) $\Delta = 2000 \text{ cm}^{-1}$, (4) $\Delta = 3000 \text{ cm}^{-1}$, (5) $\Delta = 4000 \text{ cm}^{-1}$.

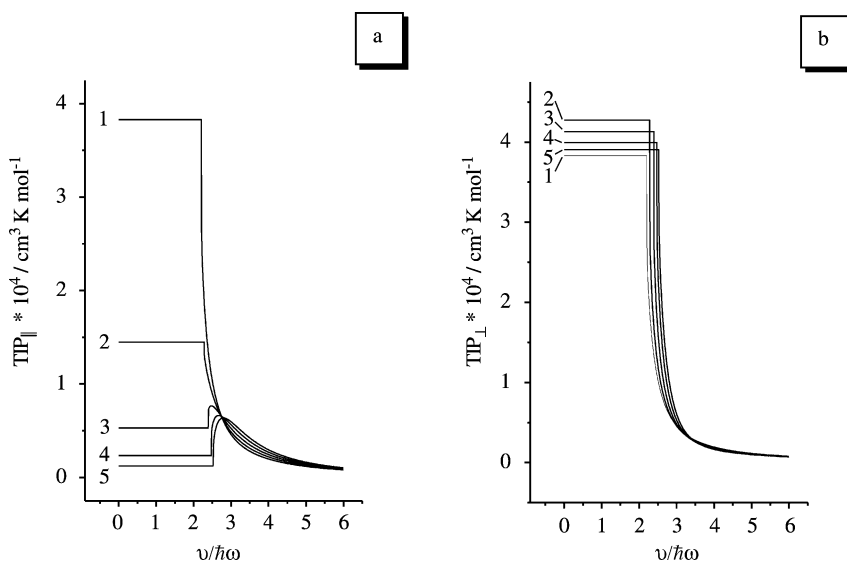


Fig. 5. Calculated principal values of TIP as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = -1000 \text{ cm}^{-1}$, (3) $\Delta = -2000 \text{ cm}^{-1}$, (4) $\Delta = -3000 \text{ cm}^{-1}$, (5) $\Delta = -4000 \text{ cm}^{-1}$.

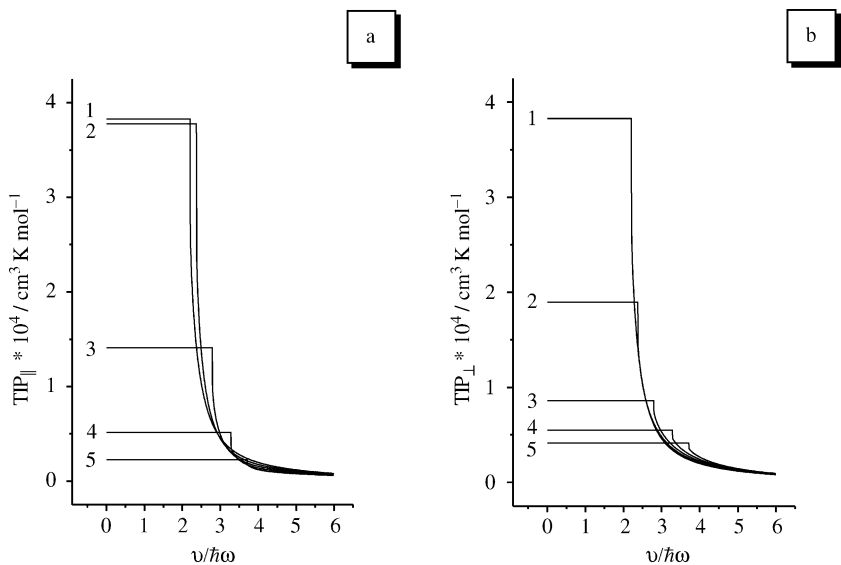


Fig. 6. Calculated principal values of TIP as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = 1000 \text{ cm}^{-1}$, (3) $\Delta = 2000 \text{ cm}^{-1}$, (4) $\Delta = 3000 \text{ cm}^{-1}$, (5) $\Delta = 4000 \text{ cm}^{-1}$.

from the unquenched axial part of the spin–orbital interaction. For higher values of the vibronic constants when the ground adiabatic surface has three minima both components of TIP turn to zero. For positive values of the crystal field TIP_{\parallel} and TIP_{\perp} behave in a similar manner, namely, they demonstrate a strong decrease with the increase of Δ .

The behavior of the TIP_{\parallel} and TIP_{\perp} contributions in all cases is closely interrelated with that of the g -factors. The same physical reasons, i.e., the strength of the PJT effect (efficiency of the mixing of the ground and excited states) form the basis of such a behavior.

6. CONCLUDING REMARKS

In this chapter we have discussed the magnetic properties of the low-spin d^5 -ion in octahedral and quasi-octahedral ligand coordination. The developed model involves all relevant electronic interactions (the strong cubic crystal field, the spin–orbital splitting of the ground 2T_2 -state and the trigonal crystal field) as well as the vibronic coupling with the tetragonal vibrations that leads to the PJT effect. These interactions were shown to determine the magnetic characteristics, namely, the parallel and perpendicular components of the g -factor and TIP. The efficiency of mixing of two Kramers doublets (ground and excited) by the tetragonal modes active in PJT plays a crucial role in the magnetic anisotropy of the system. At the same time the trigonal crystal field facilitates or suppresses this mixing resulting thus either in the appreciable anisotropy or in the fully isotropic behavior.

This chapter is the first step in the study of the magnetic behavior of the complexes of 5d-ions. The model is based on the Born–Oppenheimer version of the adiabatic approximation, i.e., only the minima of the lower adiabatic surfaces are taken into account while calculating g -factors and TIP.

The validity conditions for the semiclassical adiabatic approach in the description of the systems with orbitally non-degenerate levels are elucidated in the basic works of Born and Oppenheimer (comprehensive discussion can be found in Refs. [6,7]). In these systems, the slow nuclear motion can be separated from the fast electronic one. The situation is quite different in the JT systems where, in general, this separation is impossible due to hybridization of the electronic and vibrational states. Nevertheless, in many important cases the adiabatic approach can serve as a relatively simple and at the same time powerful tool for the theoretical study of the JT systems giving accurate quantitative results and clear insight on the physical nature of the physical phenomena.

The question of the applicability of the semiclassical adiabatic approach to the vibronic problems in the JT systems is rather complicated in general and the thorough answer can be done with regard to a particular problem. In our brief discussion of this question we will refer to two areas – thermodynamic properties and resonance (optical) problems. In Ref. [9] the magnetic properties of mixed-valence dimeric and trimeric clusters are considered in the framework of

the PJT model with due account of Heisenberg exchange and double exchange. The results of the semiclassical calculations of the magnetic moments vs. temperature were carefully tested by comparison with quantum-mechanical results. The results exhibit surprisingly high accuracy of the semiclassical theory in a wide range of the temperature and coupling parameters (the worst error is less than 0.03%). The qualitative difference in the estimation of magnetic behavior between the semiclassical and dynamic approaches was intentionally found for a specific choice of the parameters when the ground vibronic levels belonging to different spin values are close. One can believe that this conclusion is common for the thermodynamic (non-resonance) characteristics of the JT systems that are defined exceptionally by the partition function.

On the contrary, the semiclassical approach in the problem of the optical absorption is restricted to a great extent and the adequate description of the phonon-assisted optical bands with a complicated structure caused by the dynamic JTE cannot be done in the framework of this approach [13]. An expressive example is represented by the two-humped absorption band of $A \rightarrow E \otimes e$ transition. The dip of absorption curve for $A \rightarrow E \otimes e$ transition to zero has no physical meaning because of the invalidity of the semiclassical approximation for this spectral range due to essentially quantum nature of the density of the vibronic states in the conical intersection of the adiabatic surface. This result is peculiar for the resonance (optical) phenomena in JT systems; full discussion of the condition of the applicability of the adiabatic approximation is given in Ref. [13].

Keeping in mind these results, in the present study we shall take advantage of the semiclassical adiabatic approach that seems to be rather good in the case of strong vibronic coupling. When the vibronic coupling is moderate the model provides less accuracy. However, even in this case it leads to a qualitatively adequate description of the magnetic properties and reasonable accuracy of the quantitative results. More exact treatment demands the solution of the dynamic PJT vibronic problem. The plateau discovered in the curves of TIP and g vs. vibronic coupling parameter is expected to exist also in the dynamic model but the stepwise behavior will change into stepless due to more smoothed distribution of nuclear configurations in the quantum-mechanical approach.

Using the developed model we are going to study two low-spin Re(II) compounds of the formulas $[\text{Re}(\text{triphos})(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$ (compound **1**) and $[\text{Et}_4\text{N}][\text{Re}(\text{triphos})(\text{CN})_3]$ (compound **2**) containing the tripodal phosphine ligand $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ 1,1,1-tris(diphenylphosphinomethyl)ethane; abbreviated triphos). In both compounds the nearest quasi-octahedral ligand environment of the Re(II)-ion can be regarded approximately as the trigonal system belonging to the C_{3v} -symmetry group. The C_3 axis passes through the triangular face composed from the phosphorous ions and another face containing three nitrogen ions in compound **1** and three carbon atoms in compound **2**. Experimentally found effective magnetic moments 1.53 and 1.28 BM are lower than the pure spin $-\frac{1}{2}$ value 1.73 BM. At the same time TIP contributions to χ are 1.796×10^{-3} and 1.363×10^{-3} for compounds

1 and **2**, respectively. These values are one order of magnitude larger than the typical TIP values in the 3d-ions.

Interpretation of this unusual magnetic behavior requires consideration also of the terms arising from the excited electronic configurations (t_2^4e , $t_2^3e^2$, etc.). Along with the interactions so far considered the magnetic contribution coming from these states is expected to be of primary importance when the TIP is significant. This work is in progress.

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