Nonradiative relaxation in spin-crossover molecules: consideration of the frequency effect

Nonradiative relaxation in spin-crossover molecules: consideration of the frequency effect

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Abstract
A model of nonradiative transitions in spin-crossover molecules is developed.
The model takes into account linear and quadratic terms of electron–vibrational
interaction. The frequency effect is shown to arise from the quadratic term of
this interaction. With account of the frequency effect analytical expressions are
derived for the multiphonon decay rate of the high-spin state of a spin-crossover
molecule. In the framework of the suggested model for different temperatures
the probability of the nonradiative decay of the high-spin Fe(II) state in the
diluted $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$, $x = 0.1$ system is calculated. The theoretical
results are in agreement with the experimental ones.

1. Introduction

The problem of nonradiative transitions is one of the fascinating problems of molecular and
solid state physics. The scientific interest of this problem is promoted by the role of nonradiative
transitions in different observed phenomena. Luminescence quenching, recombination of
electrons with local centres and holes, inelastic scattering of the current carriers by local centres
and exciton disintegration should be referred to nonradiative transitions. It is well known that
the probabilities of nonradiative transitions are the key parameters of laser generation. These
transitions also play a crucial role in different biophysical transformations. With the discovery
of the LIESST effect [1, 2] in spin-crossover systems and the elucidation of the mechanism
of light-induced population of metastable high-spin (hs) states, new possibilities to study the
high-spin–low-spin (ls) relaxation in the solid were opened.

Laser and spin-crossover systems gave rise to a new trend in the theory of nonradiative
relaxation [3, 4]. In these systems the transitions may occur between electronic states with
different spin multiplicity, for example transition $^4T_{2g}(t_2^2e) \rightarrow ^2T_{1g}(t_2^3)$ in ruby and tran-
sition $^5T_2(t_2^4e^2) \rightarrow ^1A_{1g}(t_2^6)$ in iron spin-crossover systems. That is why in [3] and [4] the
spin–orbital interaction was taken as the perturbation causing the nonradiative transition. Nev-
ertheless, in [3] and [4], as in most papers devoted to the problem of nonradiative transitions
in systems with strong electron–vibrational interaction, only the linear term of this interaction
was included in the Hamiltonian. Unfortunately, within the limits of an article it is impossible
to quote all papers based on this approximation. In the theory of nonradiative relaxation the

common action of linear and quadratic electron–vibrational interactions accompanied by the frequency effect has not been considered yet. Meanwhile, in spin-crossover systems as shown below the quadratic electron–vibrational interaction is responsible for the appreciable frequency change under the hs → ls transition and significantly affects the rates of the transitions.

Below we suggest a new model of nonradiative transitions in isolated spin-crossover systems. The model takes into account the interaction of a molecule with the crystal field, the linear and quadratic terms of electron–vibrational interaction as well as the frequency effect induced by the quadratic interaction. Within the framework of the suggested model a special emphasis will be put on the quantitative interpretation of experimental data on diluted spin-crossover $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ ($x = 0.1$) compounds [5].

The paper is organized as follows. In section 2 the quantum mechanical theory of non-radiative transitions in spin-crossover molecules is developed. The theory takes into account the effects of linear and quadratic terms of electron–vibrational interaction on the rates of non-radiative transitions. In section 3 the calculation of the matrix elements of the perturbation operator is carried out. The comparison of theoretical and experimental results on $[Zn_{1-x}Fe_x(ptz)_6]$ $(BF_4)_2$ ($x = 0.1$) systems is given in section 4.

2. Theory

We start with the model of nonradiative transitions in a single-spin-crossover molecule. The Hamiltonian of an isolated molecule can be presented as:

$$H = H_e + H_L + H_{ev} \tag{1}$$

where the first term is the electronic Hamiltonian determining the wavefunctions and the eigenvalues of a molecule in the fixed nuclear configuration. The Hamiltonian H_e involves the kinetic and potential energies of all d electrons, their interelectronic repulsion as well as their interaction with the crystal surrounding. H_L represents the Hamiltonian of free lattice vibrations and H_{ev} is the vibronic interaction Hamiltonian.

The spin-crossover transformation is usually characterized by a sizeable elongation in the metal to ligand bond length [6]. The change of the equilibrium distances evidences a strong interaction of the transition metal ion with the displacements of the nearest surroundings. However, in most cases in neat solid state systems the spin-crossover transition is not accompanied by a structural phase transition. So a conclusion can be made [7, 8] that the contribution of non-symmetric Jahn–Teller modes to the vibronic Hamiltonian is small. At the same time, infrared and Raman spectroscopy data indicate different vibrational frequencies in the low-spin (ls) and high-spin (hs) states of a crossover complex (see, for example, [9]). The so-called frequency effect [10] is usually referred to the quadratic terms of electron–vibrational interaction. Therefore, we further confine ourselves to a simplified vibronic model with accounting only of the local full-symmetric (breathing) A_1 mode. In the operator of electron–vibrational interaction we include both the linear and quadratic terms:

$$H_{ev} = v(\vec{r})q + w(\vec{r})q^2 \tag{2}$$

where $\vec{r}$ denotes the set of electronic variables, q is the fully symmetric vibrational coordinate.

For the initial (hs) and final (ls) states of the nonradiative transition we introduce the irreducible representations Γ_1 and Γ_2 of the metal centre point group with γ_1 and γ_2 being their row indices. As long as we neglect the effect of non-symmetric vibrations further we employ the standard method of adiabatic approximation for both the hs and ls states. Within the framework of this approximation in the basis of Condon electronic wavefunctions [10] $|S_1 M_1 \Gamma_1 \gamma_1\rangle$ and $|S_2 M_2 \Gamma_2 \gamma_2\rangle$ (where S_1 and S_2 are the spins of the hs and ls states, respectively,

and M_1, M_2 are their projections) the matrix H of the molecule has the form:

$$H = \begin{pmatrix} \Delta \hat{I}_1 & 0 \\ 0 & 0 \end{pmatrix} + q \begin{pmatrix} v_1 \hat{I}_1 & 0 \\ 0 & v_2 \hat{I}_2 \end{pmatrix} + q_2 \begin{pmatrix} w_1 \hat{I}_1 & 0 \\ 0 & w_2 \hat{I}_2 \end{pmatrix} + \frac{\hbar \omega}{2} \left(q^2 - \frac{\partial^2}{\partial q^2} \right) \tag{3}$$

where v_1, w_1 and v_2, w_2 are the vibronic coupling constants for the hs- and ls-states, respectively. Δ is the electronic gap between these states, ω is the vibrational frequency, $\hat{I}_1$ and $\hat{I}_2$ are the unit matrices acting in the hs and ls spaces. The Hamiltonian H is valid when the non-adiabaticity is small and hence, our analysis is valid when the energy barrier between the spin states is large relative to $\hbar \omega$. After employing the adiabatic approximation the operators $v(\vec{r})$ and $w(\vec{r})$ are redetermined due to the account of the second order corrections on linear electron–vibrational interaction to the energies of the 'self-consistent' electronic states [10]. We retain the notations for the values v_i and w_i. Then we introduce the transformation

$$Q_i = \alpha_i^{-1} q + \frac{\alpha_i v_i}{\hbar \omega_i}$$

$$\alpha_i^{-1/4} = 1 + \frac{2 w_i}{\omega} \tag{4}$$

$$\frac{\hbar \omega_i}{2} = \sqrt{\frac{\hbar \omega}{2} \left(\frac{\hbar \omega}{2} + w_i \right)}. \tag{5}$$

The vibrational coordinate Q_i becomes dependent on the electronic state. After substitutions (4) in (3) we obtain that each state of the system is described by a Hamiltonian of the oscillator form:

$$H_i = J_i + \frac{\hbar \omega_i}{2} \left[(Q_i)^2 - \frac{\partial^2}{\partial (Q_i)^2} \right] \tag{6}$$

where

$$J_i = \Delta_i - \frac{1}{2} \frac{(v_i \alpha_i)^2}{\hbar \omega_i} \tag{7}$$

$$\Delta_1 = \Delta \qquad \Delta_2 = 0.$$

The wavefunctions of the system have the form:

$$\Psi_{i \gamma_i, n} = |S_i M_i \Gamma_i \gamma_i \rangle \Phi_n(Q_i). \tag{8}$$

The corresponding eigenvalues of the Hamiltonians H_i turn out to be equal to:

$$E_{i \gamma_i, n} = J_i + \hbar \omega_i (n + \tfrac{1}{2}). \tag{9}$$

The quadratic electron–vibrational interaction redetermines the frequency of the fully symmetric vibration. The frequency and, correspondingly, the distances between the vibrational levels become dependent on the electronic state of the molecule. Now we derive the formula for the rate of a nonradiative transition between two states with different spin values. According to [11] the excitation transfer between two discrete electron–vibrational levels $E_{1 \gamma_1, n}$ and $E_{2 \gamma_2, n'}$ is possible due to the relaxation of the final state and occurs with the rate:

$$W_{1 \gamma_1 M_1, n \rightarrow 2 \gamma_2 M_2, n'} = \frac{2}{\hbar^2} \frac{\gamma |\langle S_1 M_1 \Gamma_1 \gamma_1 | U | S_2 M_2 \Gamma_2 \gamma_2 \rangle|^2 (S_{n'n})^2}{(E_{2 \gamma_2, n'} - E_{1 \gamma_1, n})^2 + \gamma^2} \tag{10}$$

where γ^{-1} is the relaxation lifetime of the final state,

$$S_{n'n} = \int_{-\infty}^{\infty} dq \, \Phi_{n'} \left(\alpha_2 q + \frac{v_2 \alpha_2}{\hbar \omega_2} \right) \Phi_n \left(\alpha_1 q_1 + \frac{v_1 \alpha_1}{\hbar \omega_1} \right) \tag{11}$$

is the Condon integral, U is the perturbation operator acting in the electronic subsystem.

For vibrational frequencies which belong, as in the examined case, to the discrete spectrum the decay of the final $2\gamma_2$, n' state may occur on account, for instance, of anharmonic processes etc. The electron–vibrational state $2\gamma_2$, n' actually plays the role of a virtual state. The real final state is reached after relaxation. For crystal modes (continuous spectrum) the Lorentzian should be substituted by the δ-function, and the integration over the final states should be carried out.

The rate of the nonradiative decay averaged over the populations of the initial levels and summed up over the final states has the form:

$$W(1 \rightarrow 2) = \frac{1}{(2S_1 + 1)g(\Gamma_1)} \sum_{M_1, M_2, \gamma_1, \gamma_2, n, n'} W_{1\gamma_1 M_1, n \rightarrow 2\gamma_2 M_2, n'} \rho(n) \qquad (12)$$

where

$$\rho(n) = 2 \sinh\left(\frac{\beta_1}{2}\right) \exp(-\beta_1(n + 1/2))$$

is the equilibrium statistical weight of the vibrational n-state, $\beta_1 = \hbar\omega_1/kT$, $g(\Gamma_1)$ is the electronic degeneracy of the initial Γ_1-state. Equation (12) also contains the summation over the equivalent minima of the adiabatic potential sheets in the initial and final electronic states.

For the calculation of the transition rate $W(1 \rightarrow 2)$ we employ the identity

$$F(\omega_2(n' + 1/2) - \omega_1(n + 1/2)) = \int_{-\infty}^{\infty} F(\rho)\delta(\rho + \omega_1(n + 1/2) - \omega_2(n' + 1/2)) \, d\rho$$

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} F(\rho) \, d\rho \, \text{Re} \int_0^{\infty} dt \exp[-i\rho t - it(\omega_1(n + 1/2) - \omega_2(n' + 1/2))]. \quad (13)$$

With the aid of equation (13) after simple transformations equation (12) is rewritten in the form:

$$W(1 \rightarrow 2) = \frac{2\gamma}{(2S_1 + 1)g(\Gamma_1)\hbar^2}\zeta^2 \text{Re} \int_0^{\infty} \exp(-\gamma t) \, dt \left\langle \exp\left(\frac{iH_2 t}{\hbar}\right) \exp\left(\frac{-iH_1 t}{\hbar}\right) \right\rangle_s \quad (14)$$

where

$$\langle A \rangle_s = (Z_{1v})^{-1} \text{Tr}_v[\exp(-\lambda H_1)A] \qquad \left(\lambda = \frac{1}{kT}\right) \qquad (15)$$

is the statistical average upon the phonon states corresponding to the initial hs electronic state, Z_{1v} is the statistical sum of the phonon subsystem of the hs electronic state,

$$\zeta^2 = \sum_{M_1, M_2, \gamma_1, \gamma_2} |\langle S_1 M_1 \Gamma_1 \gamma_1 | U | S_2 M_2 \Gamma_2 \gamma_2 \rangle|^2.$$

The phonon statistical average in (14) is carried out by the method of cumulant expansion [10, 12]. The thus-obtained expression for the rate $W(1 \rightarrow 2)$ appears as follows:

$$W(1 \rightarrow 2) = \frac{2}{\hbar^2(2S_1 + 1)g(\Gamma_1)}\zeta^2 \text{Re} \int_0^{\infty} \exp(-\gamma t) \exp(g(t)) \qquad (16)$$

$$g(t) = -it\bar{\Delta} - \frac{1}{2}\frac{\Delta_{hl}^2}{(\hbar\omega_1)^2} \coth\left(\frac{\beta_1}{2}\right) + \frac{1}{2}\frac{\Delta_{hl}^2}{(\hbar\omega_1)^2}\frac{\cos(\omega_1 t - i\beta_1/2)}{\sinh(\beta_1/2)} \qquad (17)$$

where

$$\omega_{hl} = \frac{J_1 - J_2}{\hbar} \qquad \bar{\Delta} = \omega_{hl} + \frac{C_{hl}}{2\hbar}\coth\left(\frac{\beta_1}{2}\right)$$

$$C_{hl} = \frac{(\hbar\omega_1)^2 - (\hbar\omega_2)^2}{2\hbar\omega_1}$$

$$\Delta_{hl} = \alpha_1\left(v_2\frac{\omega_1}{\omega_2} - v_1\right). \qquad (18)$$

In equation (17) the linear terms of electron–vibrational interaction are accounted for exactly in all orders of the perturbation theory, while the quadratic terms only in the first order. This approximation is valid as long as $C_{hl} \ll \Delta_{hl}$. We employ further the generating function of the modified Bessel functions in the form:

$$\exp(z \cos \varphi) = \sum_{n=-\infty}^{\infty} \exp(in\varphi) I_n(z). \tag{19}$$

Substituting equation (19) in equation (17), and then carrying out the integration over t in (16) we obtain:

$$W(1 \to 2) = \frac{2}{\hbar^2 (2S_1 + 1) g(\Gamma_1)} \zeta^2 \sum_n I_n \left(\frac{\Delta_{hl}^2}{2(\hbar\omega_1)^2 \sinh(\beta_1/2)} \right) \exp \left(\frac{n\beta_1}{2} \right)$$
$$\times \exp \left(-\frac{\Delta_{hl}^2 \coth(\beta_1/2)}{2(\hbar\omega_1)^2} \right) \frac{\gamma}{\gamma^2 + (\bar{\Delta} - n\omega_1)^2} \tag{20}$$

where the summation over n includes all channels of multiphonon decay of the hs state conforming with the energy conservation law. Nevertheless, for temperatures $kT < \hbar\omega_1$ the contribution of terms with $n < 0$ (virtual absorption of vibrational quanta) can be neglected. These transitions should be taken into account beginning with the temperatures for which $\bar{n}(\omega_1) + 1 \sim \bar{n}(\omega_1)$. For $kT < \hbar\omega_1$ the rate of decay (20) can be presented as a sum of probabilities of partial processes each of which corresponds to a hs $\to$ ls transition with the emission of a definite number of vibrational quanta. The maximum value of the number n is denoted by $\bar{n}$ and determined by the inequality $|\bar{\Delta} - \bar{n}\omega_1| < \omega_1$. So $\bar{n}$ is approximately equal to $[\bar{\Delta}/\omega_1]$ (where the symbol [] indicates the integer part of the quantity $\bar{\Delta}/\omega_1$). The value $[\bar{\Delta}/\omega_1]$ depends on the vibrational frequency of the hs state and not on the mean value of the frequencies ω_1 and ω_2. Formula (20) for the rate $W(1 \to 2)$ differs from the usually accepted one at several points. The change in the frequency leads to the redetermination of the so-called heat creation constant (Huang–Rhys factor)

$$S = \frac{\Delta_{hl}^2}{2(\hbar\omega_1)^2}. \tag{21}$$

In terms of the equilibrium values $Q_i^{(e)} = -v_i \alpha_i / \hbar\omega_i$ of the vibrational coordinates $Q_i (i = 1, 2)$, S is written as:

$$S = \frac{1}{2} \left(Q_1^e - \frac{\alpha_2}{\alpha_1} \frac{\omega_2}{\omega_1} Q_2^e \right) \tag{22}$$

and depends not only on the vibronic parameters v_1 and v_2 but also on the ratio of the frequencies ω_1 and ω_2. For equal frequencies $\omega_1 = \omega_2 = \omega$ equation (22) passes to its usually accepted form:

$$S_o = \tfrac{1}{2} Q_{hl}^2 \qquad Q_{hl}^e = Q_1^e - Q_2^e. \tag{23}$$

In the case of $\omega_1 < \omega_2$, the so called frequency effect also gives rise to the temperature decrease of the energy gap between the minima of the adiabatic potential sheets of the hs and ls states (term $(C_{hl}/2\hbar) \coth(\beta_1/2)$ in $\bar{\Delta}$, equation (18)). It is worth noting that taking account of the final state width each term in equation (20) describes a Lorentz line corresponding to a transition accompanied by the generation of n vibrational quanta. For low temperatures $S/\sinh(\beta_1/2) \ll 1$, equation (20) takes on the form

$$W(1 \to 2) = \frac{2 \exp(-S)}{\hbar^2 (2S_1 + 1) g(\Gamma_1)} \zeta^2 \sum_n \frac{S^n}{n!} \frac{\gamma}{\gamma^2 + (\bar{\Delta} - n\omega_1)^2}. \tag{24}$$

If all processes with emission and absorption of vibrational quanta are accounted for, and n is considered as a continuous variable ($-\infty \leqslant n \leqslant \infty$, see equation (19)) for $\gamma \to 0$ the Lorentzian can be replaced by the δ-function, and the integration over n gives:

$$W(1 \to 2) = \frac{2\pi\zeta^2}{\hbar^2(2S_1+1)g(\Gamma_1)\omega_1} \exp\left(\frac{\bar{n}\beta_1}{2}\right) I_{\bar{n}}\left(\frac{S}{\sinh(\beta_1/2)}\right) \exp\left(-S \coth\left(\frac{\beta_1}{2}\right)\right) \quad (25)$$

where also $\bar{n} = [\bar{\Delta}/\omega_1]$.

Equation (25) looks like that obtained in [4]. Nevertheless it accounts for two vibrational modes, and therefore the heat creation factor is given by equation (21), and the temperature dependence of the transition rate is determined by the frequency of the initial hs state. It should also be mentioned that while deriving the formula for the rate of the nonradiative hs $\to$ ls transition in [4] the average over the initial states was not carried out correctly, and therefore the factor $(2S_1+1)g(\Gamma_1)$ was missing. For example, for the hs $\to$ ls transition ($^5T_2 \to {}^1A_1$) in Fe(II) this is a factor of 15. At high temperatures we expand the functions $g(t)$ over t and retain terms from the zeroth to the second order inclusive

$$g(t) = -it\bar{\Delta} + \frac{it}{2}\frac{\Delta_{hl}^2}{\hbar^2\omega_1} - \frac{t^2}{4}\frac{\Delta_{hl}^2}{\hbar^2} \coth\left(\frac{\beta_1}{2}\right). \quad (26)$$

For

$$\hbar\gamma < |\Delta_{hl}|\sqrt{\coth\left(\frac{\beta_1}{2}\right)}$$

and

$$\left|\hbar\omega_{hl} + \frac{C_{hl}}{2}\coth\left(\frac{\beta_1}{2}\right) - \frac{\Delta_{hl}^2}{2\hbar\omega_1}\right| < |\Delta_{hl}|\sqrt{\coth\left(\frac{\beta_1}{2}\right)}$$

after integration over t in equation (16) we obtain

$$W(1 \to 2) = \frac{2\zeta^2}{\hbar^2(2S_1+1)g(\Gamma_1)}\sqrt{\frac{\pi\hbar^2}{(\Delta_{hl})^2\coth(\beta_1/2)}}\exp\left(-\frac{\hbar(\bar{\Delta}-(\Delta_{hl})^2/2\hbar^2\omega_1)^2}{(\Delta_{hl})^2\coth(\beta_1/2)}\right). \quad (27)$$

For extremely high temperatures $kT \gg \hbar\omega_1$ the nonradiative transition has an activation character

$$W(1 \to 2) \sim \exp\left(-\frac{\hbar^2(\bar{\Delta}-(\Delta_{hl})^2/2\hbar^2\omega_1)^2\hbar\omega_1}{2(\Delta_{hl})^2 kT}\right). \quad (28)$$

Below, it will be shown that for spin-crossover systems the criteria of application of equations (27), (28) are not fulfilled for any reasonable temperature.

3. Calculation of the matrix elements of the perturbation operator

Now we shall consider the factor ζ^2 that enters the expression for the transition rate. As long as the initial and final states of the nonradiative transition possess different spin multiplicities as in [3, 4] the operator of spin–orbital interaction H_{SO} is assumed to promote the transition. Further we shall examine the hs–ls transition in the Fe(II) ion and restrict ourselves to a cubic octahedral environment of this ion. Under this assumption the hs–ls transition is identified with that between the states $^5T_2(t_2^4 e^2)$ and $^1A_1(t_2^6)$. However, the spin–orbital interaction has vanishing matrix elements between these two terms and couples only each of them to the state 3T1 arising from the configuration $t_2{}^5e$. In such a way only in the second order of the

perturbation theory a nonvanishing matrix element of the operator of spin–orbital interaction appears:

$$\langle {}^5T_2\,\gamma_1 M_1|U|{}^1A_1\gamma_2 M_2\rangle$$

$$= -\left(\frac{1}{\Delta E_1}+\frac{1}{\Delta E_2}\right)\sum_{\gamma_3 M_3}\langle {}^5T_2\,\gamma_1 M_1|H_{SO}|{}^3T\gamma_3 M_3\rangle\langle {}^3T_1\gamma_3 M_3|H_{SO}|{}^1A_1\gamma_2 M_2\rangle$$

$$(29)$$

where $\Delta E_1 = E_{{}^3T_1} - E_{{}^5T_2}$ is the energy gap between the states ${}^5T_2$ and ${}^3T_1$ at the equilibrium configuration of the state ${}^5T_2$ and $\Delta E_2 = E_{{}^3T_1} - E_{{}^1A_1}$ is the energy gap between the states ${}^1A_1$ and ${}^3T_1$ at the equilibrium configuration of the state ${}^1A_1$. For the purpose of obtaining the matrix elements of the operator H_{SO} we represent this operator in the form [13], which is valid only for a cubic point group:

$$H_{SO} = \frac{1}{\sqrt{2}}[-V_{+1\alpha}(1T_1)+iV_{+1\beta}(1T_1)] + \frac{1}{\sqrt{2}}[V_{-1\alpha}(1T_1)+iV_{-1\beta}(1T_1)] + V_{O\gamma}(1T_1) \quad (30)$$

where

$$V_{\pm 1\alpha}(1T_1) = \sum_i S_{i\pm 1}t_{i\alpha}$$

$$V_{\pm 1\beta}(1T_1) = \sum_i S_{i\pm 1}t_{i\beta}$$

$$V_{O\gamma}(1T_1) = \sum_i S_{iO}t_{i\gamma} \qquad (31)$$

$$S_{i\pm 1} = \mp\frac{1}{\sqrt{2}}(S_{ix}\pm iS_{iy})$$

$$S_{iO} = S_{iz}$$

and

$$t_{i\alpha} = \xi(\vec{r}_i)\ell_{ix} \qquad t_{i\beta} = \xi(\vec{r}_i)\ell_{iy} \qquad t_{i\gamma} = \xi(\vec{r}_i)\ell_{iz}. \qquad (32)$$

In equation (31) the summation over all d electrons of the Fe(II) ion is carried out. The operator H_{SO} is expressed as the linear combination of double tensor operators $V_{q\bar{\gamma}}(1T_1)$ where $q = 0$, ± 1, and $\bar{\gamma} = \alpha, \beta, \gamma$. For the double tensor operators $V_{q\bar{\gamma}}(1T_1)$ the Wigner–Eckart theorem leads to the formula:

$$\langle \Gamma\gamma SM|V_{q\bar{\gamma}}(1T_1)|\Gamma'\gamma' S'M'\rangle$$

$$= [(2S+1)(\Gamma)]^{-1/2}\langle \Gamma S\|V(1T_1)\|\Gamma'S'\rangle\langle SM|S'M'1q\rangle\langle \Gamma\gamma|\Gamma'\gamma' T_1\bar{\gamma}\rangle \qquad (33)$$

where $\langle \Gamma S\|V(1T_1)\|\Gamma'S'\rangle$ is the reduced matrix element, $\langle SM|S'M'1q\rangle$ and $\langle \Gamma\gamma|\Gamma'\gamma' T_1\bar{\gamma}\rangle$ are the Wigner and Clebsch–Gordon coefficients, respectively. Then with the aid of equations (29), (30) and (33) for ζ^2 (equation (14)) we obtain:

$$\zeta^2 = \frac{2}{135}\left(\frac{1}{\Delta E_1}+\frac{1}{\Delta E_2}\right)^2 |\langle {}^5T_2\|V(1T_1)\|{}^3T_1\rangle|^2|\langle {}^3T_1\|V(1T_1)\|{}^1A_1\rangle|^2. \qquad (34)$$

The multielectronic reduced matrix elements $\langle {}^5T_2\|V(1T_1)\|{}^3T_1\rangle$ and $\langle {}^3T_1\|V(1T_1)\|{}^1A_1\rangle$ can be expressed in terms of those for the one-electron system, $\langle t_2\|v(1T_1)\|e\rangle$:

$$\langle {}^5T_2\|V(1T_1)\|{}^3T_1\rangle = -\sqrt{\frac{5}{2}}\langle t_2\|v(1T_1)\|e\rangle = -3\sqrt{5}i\xi$$

$$\langle {}^3T_1\|V(1T_1)\|{}^1A_1\rangle = \langle t_2\|v(1T_1)\|{}^3T_1\rangle = 3\sqrt{2}i\xi \qquad (35)$$

where ξ is the radial integral

$$\xi = \int_0^\infty R_{3d}^2(r)\xi(r)r^2\,dr \qquad (36)$$

that is called the constant of spin–orbital coupling. While writing equations (35) and (36) we neglect the difference between the radial functions of the e and t^2 orbitals. The final result for ζ^2 appears as follows:

$$\zeta^2 = 12\xi^4 \left(\frac{1}{\Delta E_1} + \frac{1}{\Delta E_2} \right)^2. \tag{37}$$

Equation (37) differs from that obtained in [4] by a factor of 1.5. The discrepancy takes place because in [4] the matrix elements in equation (29) were replaced by their reduced values taken from [14] and the summation over the values γ_i was not carried out. Further we estimate the value ζ with the aid of experimental data on the LIESST effect in $[Fe(ptz)_6](BF_4)_2$ [6]. As the gap ΔE_2 the maximum of the $^1A_1 \rightarrow {}^3T_1$ band at $10\,280$ cm^{-1} (980 nm) is taken. The energies of the levels $^3T_2$ and ^5E are supposed to be approximately equal to $14\,300$ cm^{-1}. As long as the energy of the transition $^5T_2 \rightarrow {}^5E$ is about $12\,200$ cm^{-1} (820 nm) the electronic gap Δ between the states $^5T_2$ and $^1A_1$ is 2100 cm^{-1}. Finally, for ΔE_1 we obtain the value 8180 cm^{-1}. For $\Delta E_1 = 8180$ cm^{-1}, $\Delta E_2 = 10\,280$ cm^{-1} and $\xi = 404$ cm^{-1} [14], $\zeta^2 \approx 124^2$ cm^{-2}. If for ΔE_1 the value 6828 cm^{-1}, calculated in [15] for $[Fe(ptz)_6](BF_4)_2$, is taken, we obtain a bigger parameter $\zeta^2 \approx 137^2$ cm^{-2}. The gaps ΔE_1 and ΔE_2 in [4] were taken from the energy-level diagram of Tanabe and Sugano [16] for the d^6 ion at the crossing point $\Delta E = 7.6B$ under the assumption that $C/B = 4.81$. For $|\zeta|$ a value of 170 cm^{-1} was obtained. Nevertheless the values of B and C are different for each complex, and the energy gap between the states $^5T_2$ and $^1A_1$ is non-vanishing. From this point of view the estimation of $|\zeta|$ based on experimental data looks more precise.

4. Comparison with experiment

The numerical estimation of the nonradiative transition rate has been performed for the hs–ls transition in the mixed crystal system $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$, $x = 0.1$ [5]. In this diluted system the spin transition is gradual [5], as expected in the absence of cooperative effects. The hs–ls relaxation in $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$, $x = 0.1$ is a single-exponential function. In such a way, at different temperatures the experimental values of the probability of decay of the hs state correspond to those for a single spin-crossover molecule. As seen above, the probability of decay in an isolated molecule is governed by nine parameters. These are the vibronic parameters v_1, v_2, w_1, w_2, the frequencies ω_1, ω_2, the relaxation time γ^{-1} of the final state, the gap ω_{hl} and the constant ζ. In order to calculate the temperature dependence of the decay rate first we will try to evaluate and discuss the values of the above mentioned parameters. For an octahedral complex formed by Fe(II) and six ligands the matrix elements v_1 and v_2 of the linear electron–vibrational interaction can be expressed as the mean values of the derivatives of the crystal field energies in the ls and hs states, respectively

$$v_1 = \langle hs| \left(\frac{\partial W(r, R)}{\partial R} \right)_{R=R_{hs}} |hs\rangle \sqrt{\frac{\hbar\omega_1}{6f_1}}$$

$$v_2 = \langle ls| \left(\frac{\partial W(r, R)}{\partial R} \right)_{R=R_{ls}} |ls\rangle \sqrt{\frac{\hbar\omega_2}{6f_2}}. \tag{38}$$

where R_{hs}, R_{ls} are the metal–ligand distances in these states, $W(r, R)$ is the potential energy of the interaction of the electrons of the iron ion with the atoms of the surroundings and f_1 and f_2 are the force constants of the full symmetric mode in the hs and ls states, respectively. In the point-charge crystal field model, $W(r, R)$ is the crystal field acting on the electronic shell

of the iron ion. If the complex FeX_6 (where X is a neutral ligand) is assumed to be cubic

$$v_1 = 4\sqrt{\frac{6\hbar\omega_1}{f_1}}\frac{Dq^{hs}}{R_{hs}}$$

$$v_2 = 24\sqrt{\frac{6\hbar\omega_2}{f_2}}\frac{Dq^{ls}}{R_{ls}} \tag{39}$$

where Dq^{hs} and Dq^{ls} are the parameters of the cubic crystal field [13] in the hs and ls states, respectively. While estimating the parameters v_1 and v_2 for Dq^{hs}, Dq^{ls}, R_{ls}, R_{hs} the values for $[Fe(ptz)_6](BF_4)_2$ listed in [18] are taken:

$$Dq^{hs} = 2055\text{ cm}^{-1} \qquad Dq^{ls} = 1176\text{ cm}^{-1}$$
$$R_{ls} = 2\text{ Å} \qquad R_{hs} = 2.2\text{ Å.} \tag{40}$$

For the fully symmetric breathing mode in $[Fe(ptz)_6](BF_4)_2$ the frequencies $\omega_1 = 161$ cm^{-1}, $\omega_2 = 200$ cm^{-1}, the force constants $f_1 = 158$ N m^{-1}, $f_2 = 227$ N m^{-1} have been determined in [17, 18] permitting us to perform the calculation of the parameter S (equation (21)). With these values for $\omega \gg w_2$ we obtain

$$S = \frac{48}{f_1\hbar\omega_1}\left(6\frac{Dq^{ls}}{R_{ls}}\sqrt{\frac{f_1\omega_1}{f_2\omega_2}} - \frac{Dq^{hs}}{R_{hs}}\right)^2 = 62.388. \tag{41}$$

The inequality $\omega \gg w_2$ seems to be reasonable because $\omega_2 > \omega_1$ and $\omega_2 - \omega_1 \ll \omega_1, \omega_2$. It is seen that equation (41) allow us to express the parameter S through the empirical parameters of the crystal field and of the phonon spectrum and to obtain the numerical evaluation of the discussed effects. At low temperatures $kT < \hbar\omega_1$ the anharmonic broadening γ of the final state of the nonradiative transition is a value of the order of 1 cm^{-1} [19]. For $|\zeta|$ we take the value 137 cm^{-1} estimated in section 2. Using the frequencies ω_1 and ω_2 [17, 18] the value C_{hl} (equation (18)) is easily calculated: it is equal to -43.7 cm-1 and small in comparison with the value $\Delta_{hl} \approx 1789$ cm^{-1}. In such a way the vibronic parameters w_1, w_2 characterizing the quadratic electron–vibrational interaction do not enter in an evident form the expression for the transition rate (see equations (20), (25)). They are contained in the theory by means of the frequencies ω_1, ω_2. From experimental data it is impossible to obtain direct information about the gap ω_{hl} between the minima of the adiabatic potential sheets corresponding to the ls and hs states insofar as the optical hs $\Leftrightarrow$ ls transitions are forbidden. Therefore the gap ω_{hl} will be considered as a fitting parameter.

In figure 1 the temperature dependence of the transition probability $W(1 \rightarrow 2)$ calculated with the aid of equations (20) and (25) is depicted; here also the experimental data of Jeftic and Hauser [5] are shown. Curves 1 and 3 obtained by means of equation (25) correspond to $\bar{n} = 4$ and 3, respectively. It is seen that the theoretical results presented in curve 3 differ from the experimental ones by an order of magnitude. In the case of $\bar{n} = 4$ up to $T = 50.2$ K the theoretical and experimental values coincide. Beginning from the temperature $T = 52.6$ K the theoretical curve lies higher.

However, in this range of temperatures the theoretical and experimental values are of the same order of magnitude. For equation (25) the choice $\bar{n} = 4$ provides a better agreement with the experiment as compared with $\bar{n} = 3$ insofar as for $S \gg 1$ the probability of the nonradiative transition turns out to be an increasing function of the number of vibrational quanta. For instance, at low temperatures the ratio of the probabilities for $\bar{n} = 4$ and $n = 3$, calculated with the aid of equation (25), is equal to $S/4 \gg 1$. As long as $\bar{n} = [\bar{\Delta}/\omega_1]$, a conclusion can be made that, for $\bar{n} = 4$, the gap $\bar{\Delta}$ falls within the limits 644 cm$^{-1} \leqslant \bar{\Delta} < 805$ cm^{-1}, and hence, the value of the gap ω_{hl} is determined by the inequality 666 cm$^{-1} \leqslant \omega < 827$ cm^{-1}.
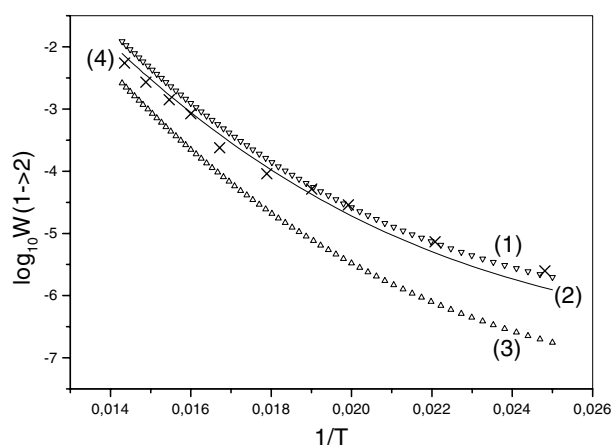
Figure 1. The probability rate $W(1 \rightarrow 2)$ as a function of temperature with $S = 62.388$, $\omega_1 = 161$ cm^{-1}, $\omega_2 = 180$ cm^{-1}, $|\zeta| = 137$ cm^{-1}. (1) (triangle down) calculated using equation (25), $\bar{n} = 4$; (2) (solid curve) calculated using equation (20), n from 0 to 3, $\omega_{hl} = 502.5$ cm^{-1}; (3) (triangle up) calculated using equation (25), $\bar{n} = 3$; (4) (crosses) experimental data [5].

Curve 2 was calculated with the aid of equation (20) for n from 0 to 3. It is obvious that starting with $T = 45.5$ K these results are in satisfactory agreement with the experimental ones. For the gap between the minima of adiabatic potential sheets of the hs and ls states, a value of 502.5 cm^{-1} is obtained. This value seems to be more reasonable as compared with the parameter $\Gamma = 170$ cm^{-1} [5] characterizing the strength of the elastic interactions and determining the temperature $T_{1/2} \cong 150$ K of the spin-crossover transition in the neat [Fe(ptz)$_6$](BF$_4$)$_2$ system.

As a matter of fact, the smaller the gap the easier the condition of spin crossover for $\Gamma = 170$ cm^{-1} is fulfilled. It is also worth noting that the numerical calculations (equation (20), curve 2) show that the term with $n = 3$ gives the dominant contribution to the transition rate $W(1 \rightarrow 2)$. Therefore, at low temperatures for the above listed values of the parameters, the ratio of the probabilities $W(1 \rightarrow 2)$ calculated with the aid of equations (20) ($n = 3$) and (25) ($\bar{n} = 4$)

$$\eta = \frac{4\gamma\omega_1}{(\gamma^2 + (\bar{\Delta} - 3\omega_1)^2)\pi S}$$

is less than 1, and for $\bar{n} = 4$ equation (25) gives higher values of $W(1 \rightarrow 2)$, that are in good agreement with experimental ones.

Neglecting the frequency effect the heat creation constant S_o equation (23) can be expressed as [6]

$$S_o = \frac{3f\Delta R_{hl}^2}{\hbar\omega_o} \tag{42}$$

where $f = (f_1 + f_2)/2$ and $\omega_o(\omega_1 + \omega_2)/2$ are the mean force constant and the mean frequency respectively, ΔR_{hl} is the change in the metal–ligand bond length. For $f = 192.5$ N m^{-1}, $\omega_o = 180.5$ cm^{-1}, $\Delta R_{hl} = 0.2$ Å, $S_o = 64.44$. The parameter S_o is a little bigger than that calculated with different force constants f_i and frequencies ω_i (see equation (41)). Nevertheless due to the factor $\exp(-S\coth(\beta/2))$ in the expressions (20) and (25) for the probability rate $W(1 \rightarrow 2)$ the obtained heat creation constant S_o will cause a higher order transition relative to the number of phonons and, hence, a higher gap ω_{hl} will fit the experimental values.

The consideration above carried out shows that equation (20) accounting for the relaxation of the final transition state gives better agreement with experiment and provides the possibility to estimate more precisely the energy gap ω_{hl}. Nevertheless, formula (25) gives the probabilities the values of the same order of magnitude and can be also useful.

Finally, we proceed to the discussion of the limits of validity of the semiclassical activation formula (28). For the above mentioned values of the parameters f_i, ω_i and $S = 62.388$, $\omega_{hl} = 502.5$ cm^{-1} we obtain that equation (28) is applicable for temperatures $T > 3280$ K. The large activation energy

$$E_{act} = \frac{\hbar^2(\bar{\Delta} - (\Delta_{hl})^2/2\hbar^2\omega_1)^2)\hbar\omega_1}{2(\Delta_{hl})^2} \simeq 2280 \text{ cm}^{-1}$$

does not allow us to apply the semiclassical approximation in the range of reasonable temperatures. In so doing the criteria of the semiclassical approximation do not hold for the considered hs–ls transition at any accessible physical temperatures.

5. Concluding remarks

Previous work on the influence of the interaction of a spin-crossover molecule with molecular vibrations on the rates of nonradiative transitions was centred on the simplest possible model of electron–vibrational interaction, i.e. on a linear interaction. Nevertheless for spin-crossover systems this simple model is not completely adequate because the hs $\Leftrightarrow$ ls transition is always accompanied by the change of the vibrational frequency (frequency effect). Here we have presented a model of nonradiative transitions in isolated spin-crossover systems that takes into account linear and quadratic electron–vibrational interaction. This interaction leads not only to the dependence of the frequency of the vibrational mode on the electronic state, but also to the change of the form of the adiabatic potentials corresponding to the hs and ls states, to the change of the vertical and horizontal shifts of these sheets. Nevertheless, the main effect of the quadratic interaction is the redetermination of the Huang–Rhys factor, which is the most important parameter characterizing the transition. So long as all enumerated effects already arise in the first order on the constant of quadratic electron–vibrational interaction, and the last is shown to be not strong ($C_{hl} \ll \Delta_{hl}$), the terms of vibronic interaction of a higher order will give only small corrections. Therefore they have not been taken into consideration.

Besides the account of quadratic interaction in this paper a new approach is developed to the problem of intracentre nonradiative transitions in the case of interaction of electronic states with molecular modes. The transition is considered as a nonradiative energy transfer between the initial and final electron–vibrational states, and the lifetime of the final state enters the expression for the transition rate. In such a way the relaxation of the final state providing the irreversibility of the transition is introduced in the theory. For the transition rates simple analytical formulae have been obtained. It is shown that all parameters inherent to the transition can be calculated microscopically or with the aid of experimental data. It should be outlined that the first observable effect due to the quadratic term in the Hamiltonian of electron–vibrational interaction is different vibrational frequencies in the ls and hs states. This is the effect observed by Raman [9] and infrared spectroscopy and accounted for in our model. The second observable effect of quadratic interaction is the sufficiently steep temperature dependence of the decay rate determined by the vibrational frequency of the hs state, which is smaller than that in the ls state.

In addition to the quantum theory of the non-radiative transitions, taking into account linear and quadratic electron–vibrational interaction, the semiclassical approximation is considered. The limitation and range of validity of this method are carefully explored. In particular, it

is found that for spin-crossover systems this approximation does not work in the range of reasonable temperatures.

The suggested theory was applied to the calculation of the temperature dependence of the lifetime of the hs level of the Fe(II) ion in the diluted $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$, $x = 0.1$ system. The calculated values are in satisfactory agreement with the experimental ones.

Finally, it should be mentioned that the model is restricted to a spin-crossover molecule, the symmetry of which is sufficiently high and admits only one fully symmetric vibration. In real systems the symmetry is lower and leads to several vibrations of such a type. However, from the point of view of theory the generalization of the suggested model on this case will not face principal difficulties. The only point is the knowledge of detailed information about the frequencies of the above mentioned vibrations and their symmetry as well as about the Stark splitting of the hs state.

Acknowledgments

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