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Indian Journal of Physics

ISSN 0973-1458

Indian J Phys

DOI 10.1007/s12648-020-01778-4



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Electro-vibrational Ising-type model for spin crossover in binuclear molecules

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Received: 24 September 2019 / Accepted: 10 January 2020

Abstract: A spin crossover in binuclear molecule is investigated using an Ising-type model, including the intramolecular vibrations. The spin transition curve of $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$ complex which presents a two-step transition plateau is well described by the above model. We show that the equilibrium low-spin/high-spin temperature T_{eq} is independent of the vibration frequencies of the intermediate state (HS–LS or LS–HS) ω_{LHS} . In addition, a large values of LS–LS state vibration frequencies ω_{LLS} lead to an evident two-step transition plateau.

Keywords: Spin crossover; Ising-type model; Binuclear molecules; Two-step spin transition

1. Introduction

Multifunctional molecular materials have been the object of intensive research and offer promising opportunities for applications in information processing, sensors and/or displays devices [1, 2]. In this field, the molecular magnetic materials are the most important class of these materials in general and spin-crossover (SC) compounds in particular [3–5]. Theoretically, several simple models have been introduced to study these materials, among them, a variety of Ising models adapted from the well-known Ising one, such as Ising-like model to describe spin-crossover systems [6], mixed Ising model for mixed spin systems [7–11] and frustrated Ising model for spin glasses [12]. The spin-crossover compounds have been described as molecular bistable between a low-spin ground state and a long-living high-spin excited state. The transition between these two states can be achieved by external stimulus, like pressure, magnetic field, light or temperature, and this stability of the two spin states makes the spin-crossover molecules of great importance and a great potential in technological applications [1, 4, 5]. From experimental point of view, a wide range of two-step spin-crossover molecules have been synthesized and studied [13]; however, few theoretical models were able to describe the two-step spin-crossover mechanism. A first approach was to use the Ising-like

model with two sublattices, and this model is used to describe two-step spin crossover observed in some spin transition molecules [6]. In this model, the authors consider two sublattices in the mean field approximation, where the intra-sublattice exchanges are “ferromagnetic,” while the inter-sublattices are “antiferromagnetic.” The later coupling is responsible for the two-step of the spin transition. This unusual behavior of two-step spin transition was also observed in some binuclear compounds [14, 15], where their description was carried out by an extension of the previous model with a rigorous treatment of the term which represents intramolecular interactions (between the metal centers) [16].

The calorimetric measurements by Sorai and Seki [17] reveal the importance of the molecular vibrations in spin crossover. Indeed, the purely electronic models of the phenomenon lead to an underestimation of entropy change across the transition compared to those deduced from experimental measurements. This disagreement has been attributed to the effects of vibrations. When we add the vibrations to the pure electronic model, one can get an entropic change closer to the experimental values. Such model is developed for mononuclear molecules [18], the electro-vibrational Ising-type model, and gives results in excellent agreement with the experimental data, in particular the change of the entropy after the spin transition. In addition, it allows reproducing the curves of the spin transition for mononuclear molecules. Later on, the molecular vibrations are introduced in the Ising-type model for spin crossover in binuclear molecules but for the

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purpose to study the vibration-driven spin transition (equi-energy case) [19]: a situation where it allows the assessment of the conditions under which cooperative exchange interactions and the ligand field are weak enough to favor a vibration-driven mechanism for the thermal transition. On other hand, the spin-crossover phenomenon in solid state gives rise to a large variety of behaviors, the origin of this diversity is the cooperative nature of the couplings between molecules, which finds its origin in the lattice dynamics, and this leads to the so-called elastic models. These models take in consideration the vibrations by introducing the coupling between the electronic spin states of the molecule and the lattice crystalline properties [20–22]. In the present paper, we demonstrate the role of vibrations in the spin crossover in binuclear molecules in a general manner. Therefore, the introduction of the vibrations in the model leads to the appearance of vibrational degeneracies in the partition function. Such degeneracies are so important in almost cases and lead to considerable contribution to the entropy change after transition compared to that of the pure electronic one. These additional degeneracies have also effects on equilibrium temperature and the shape of the transition curves. They permute to determine reasonable and justified values to the parameters of the model, by fitting the theoretical curves of the calculated spin transition to the experimental ones. So, after introducing the model, we used it to describe the spin crossover of the compound $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$, which is the subject of several experimental studies [14, 15].

2. Ising-type model with vibrations for binuclear molecules

A binuclear spin conversion compounds are molecules containing two metallic centers which can assume two spin states either a low or high spin. The spin state is controlled by the ligand surrounding the metallic center.

Within the electro-vibrational model which describes the two-step spin transition in symmetric binuclear molecules where the two metallic centers can be in two different spin states and therefore define two different sublattices (*A*) and (*B*), we treat the intermolecular interactions in the context of the mean field approximation, while the intramolecular term is treated exactly. The vibrations of each molecule are represented by p unidimensional harmonics oscillators. The Hamiltonian associated with a single molecule is written [19]:

$$H_m = \frac{\Delta}{2}(\sigma_A + \sigma_B) + J(\sigma_A \langle \sigma_A \rangle + \sigma_B \langle \sigma_B \rangle) + J'(\sigma_A \langle \sigma_B \rangle + \sigma_B \langle \sigma_A \rangle) + J_{AB}\sigma_A\sigma_B + \sum_{j=1}^p \text{vib} H_m^{(j)} \quad (1)$$

where σ_A and σ_B are the two fictitious spin operators equal to $+1$ in the HS state and -1 in the LS state. $J = J_{AA} = J_{BB} < 0$ is the intra-sublattice interactions, $J' = J_{AB}^{\text{intermol}} < 0$ is the inter-sublattice interactions for metallic centers belonging to different molecules, and $J_{AB} > 0$ is the intramolecular interactions.

$\sum_{j=1}^p \text{vib} H_m^{(j)}$ is the sub-Hamiltonian representing all the intramolecular vibrations, where $\text{vib} H_m^{(j)}$ represents the harmonic oscillator (j) of frequencies:

$$\begin{aligned} \omega_{\text{LLS}}^{(j)} &\rightarrow \text{state } |-, -\rangle : (\text{LS} - \text{LS}) \\ \omega_{\text{LHS}}^{(j)} &\rightarrow \text{state } |\mp, \pm\rangle : \begin{cases} (\text{LS} - \text{HS}) \\ (\text{HS} - \text{LS}) \end{cases} \\ \omega_{\text{HHS}}^{(j)} &\rightarrow \text{state } |+, +\rangle : (\text{HS} - \text{HS}) \end{aligned} \quad (2)$$

each state of the molecule is represented by a ket: $|\sigma_A, \sigma_B; n_1, n_2, \dots, n_p\rangle$, such as:

$$\begin{aligned} \sum_{j=1}^p \text{vib} H_m^{(j)} |-, -; n_1, n_2, \dots, n_p\rangle &= \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{LLS}}^{(j)} |-, -; n_1, n_2, \dots, n_p\rangle \\ \sum_{j=1}^p \text{vib} H_m^{(j)} |\mp, \pm; n_1, n_2, \dots, n_p\rangle &= \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{LHS}}^{(j)} |\mp, \pm; n_1, n_2, \dots, n_p\rangle \\ \sum_{j=1}^p \text{vib} H_m^{(j)} |+, +; n_1, n_2, \dots, n_p\rangle &= \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{HHS}}^{(j)} |+, +; n_1, n_2, \dots, n_p\rangle \end{aligned} \quad (3)$$

where $n_j = 1, 2, 3, \dots$

The total Hamiltonian of a system of N molecules, if we consider all molecules which have the same modes of vibrations, is:

$$H = \sum_{m=1}^N H_m = \sum_{m=1}^N \left[\begin{aligned} &\frac{\Delta}{2}(\sigma_A + \sigma_B) + J(\sigma_A \langle \sigma_A \rangle \\ &+ \sigma_B \langle \sigma_B \rangle) + J'(\sigma_A \langle \sigma_B \rangle \\ &+ \sigma_B \langle \sigma_A \rangle) + J_{AB}\sigma_A\sigma_B \end{aligned} \right] + N \sum_{j=1}^p \text{vib} H_m^{(j)} \quad (4)$$

The Hamiltonian H_m has the following eigenvalues:

$$\begin{aligned}
 & \left[\begin{aligned} & (-\Delta - (J + J')(\langle \sigma_A \rangle + \langle \sigma_B \rangle) + J_{AB}) \\ & + \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{LLS}}^{(j)} \end{aligned} \right] \rightarrow \text{states } \{|-, -\rangle\} \\
 & \left[\begin{aligned} & (\mp(J - J')(\langle \sigma_A \rangle - \langle \sigma_B \rangle) - J_{AB}) \\ & + \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{LHS}}^{(j)} \end{aligned} \right] \rightarrow \text{states } \{|\mp, \pm\rangle\} \\
 & \left[\begin{aligned} & (\Delta + (J + J')(\langle \sigma_A \rangle + \langle \sigma_B \rangle) + J_{AB}) \\ & + \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{HHS}}^{(j)} \end{aligned} \right] \rightarrow \text{states } \{|+, +\rangle\}
 \end{aligned} \tag{5}$$

The previous eigenvalues are g_{LS}^2 , $g_{\text{LS}}g_{\text{HS}}$ and g_{HS}^2 times degenerate, respectively, where g_{LS} and g_{HS} are the (electronic) degeneracies of the (LS) and (HS) states, respectively.

Within the canonical ensemble and for N identical particles, the partition function is given by:

$$Z = (Z_m)^N, \quad Z_m = \sum_{r_m} \exp(-\beta E_{r_m}) \tag{6}$$

where $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, and T is the temperature.

Z_m is the partition function of molecule (m), and r_m represents all possible states of the molecule:

$$\begin{aligned}
 Z_m = & g_{\text{LS}}^2 \exp\{+\beta(\Delta + (J + J')m - J_{AB})\} Z_{\text{vib}}^{\text{LLS}} \\
 & + g_{\text{LS}}g_{\text{HS}} \exp\{+\beta((J - J')n + J_{AB})\} Z_{\text{vib}}^{\text{LHS}} \\
 & + g_{\text{HS}}g_{\text{LS}} \exp\{-\beta((J - J')n - J_{AB})\} Z_{\text{vib}}^{\text{LHS}} \\
 & + g_{\text{HS}}^2 \exp\{-\beta(\Delta + (J + J')m + J_{AB})\} Z_{\text{vib}}^{\text{HHS}}
 \end{aligned} \tag{7}$$

where

$$\begin{aligned}
 Z_{\text{vib}}^{\text{LLS}} &= \sum_{n_j=0}^{\infty} \exp\left\{-\beta \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{LLS}}^{(j)}\right\} = \prod_{i=1}^p \frac{\exp(-\beta \frac{1}{2} \hbar \omega_{\text{LLS}}^{(i)})}{1 - \exp(-\beta \hbar \omega_{\text{LLS}}^{(i)})} \\
 Z_{\text{vib}}^{\text{LHS}} &= \sum_{n_j=0}^{\infty} \exp\left\{-\beta \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{LHS}}^{(j)}\right\} = \prod_{i=1}^p \frac{\exp(-\beta \frac{1}{2} \hbar \omega_{\text{LHS}}^{(i)})}{1 - \exp(-\beta \hbar \omega_{\text{LHS}}^{(i)})} \\
 Z_{\text{vib}}^{\text{HHS}} &= \sum_{n_j=0}^{\infty} \exp\left\{-\beta \sum_{j=1}^p \left(n_j + \frac{1}{2} \right) \hbar \omega_{\text{HHS}}^{(j)}\right\} = \prod_{i=1}^p \frac{\exp(-\beta \frac{1}{2} \hbar \omega_{\text{HHS}}^{(i)})}{1 - \exp(-\beta \hbar \omega_{\text{HHS}}^{(i)})}
 \end{aligned} \tag{8}$$

We obtain Z_m in its final form:

$$\begin{aligned}
 Z_m = & \exp(-\beta J_{AB}) [Z_{\text{vib}}^{\text{LLS}} g_{\text{LS}}^2 \exp\{+\beta[\Delta + (J + J')m]\} \\
 & + Z_{\text{vib}}^{\text{LHS}} 2g_{\text{LS}}g_{\text{HS}} \exp\{2\beta J_{AB}\} \cosh\{\beta(J - J')n\} \\
 & + Z_{\text{vib}}^{\text{HHS}} g_{\text{HS}}^2 \exp\{-\beta[\Delta + (J + J')m]\}]
 \end{aligned} \tag{9}$$

with $m = \langle \sigma_A \rangle + \langle \sigma_B \rangle$ and $n = \langle \sigma_A \rangle - \langle \sigma_B \rangle$, where

$$\begin{aligned}
 Z_{\text{vib}}^{\alpha} &= \prod_{i=1}^p Z_{\text{vib}}(\omega_{\alpha}^{(i)}, T), \\
 Z_{\text{vib}}(\omega_{\alpha}^{(i)}, T) &= \frac{1}{2 \sinh\left(\frac{1}{2}\beta \hbar \omega_{\alpha}^{(i)}\right)}
 \end{aligned} \tag{10}$$

with $\alpha = \text{LLS, LHS or HHS}$ being the contributions of the vibrations of states (LLS), (LHS) and (HHS), respectively, in the partition function of the system.

The mean magnetization of the system is given by (N identical molecules):

$$\begin{aligned}
 \langle \sigma \rangle &= \text{Tr}(\sigma e^{-\beta H})/Z = \left(\sum_r \sigma e^{-\beta H} \right) / Z \\
 &= \left(\sum_{r_m} \sigma \exp(-\beta E_{r_m}) \right) (Z_m)^{N-1} / (Z_m)^N
 \end{aligned} \tag{11}$$

So, the mean magnetization in the sublattice (A) is given by:

$$\begin{aligned}
 \langle \sigma_A \rangle = & \left[\begin{aligned} & - \exp\{\beta[\Delta + (J + J')m]\} \\ & - 2r \frac{Z_{\text{vib}}^{\text{LHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp(2\beta J_{AB}) \sinh[\beta(J - J')n] \\ & + r^2 \frac{Z_{\text{vib}}^{\text{HHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp\{-\beta[\Delta + (J + J')m]\} \end{aligned} \right] / \\
 & \left[\begin{aligned} & \exp\{\beta[\Delta + (J + J')m]\} \\ & + 2r \frac{Z_{\text{vib}}^{\text{LHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp(2\beta J_{AB}) \cosh[\beta(J - J')n] \\ & + r^2 \frac{Z_{\text{vib}}^{\text{HHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp\{-\beta[\Delta + (J + J')m]\} \end{aligned} \right]
 \end{aligned} \tag{12}$$

For the mean magnetization of sublattice (B), we have:

$$\begin{aligned}
 \langle \sigma_B \rangle = & \left[\begin{aligned} & - \exp\{\beta[\Delta + (J + J')m]\} \\ & + 2r \frac{Z_{\text{vib}}^{\text{LHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp(2\beta J_{AB}) \sinh[\beta(J - J')n] \\ & + r^2 \frac{Z_{\text{vib}}^{\text{HHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp\{-\beta[\Delta + (J + J')m]\} \end{aligned} \right] / \\
 & \left[\begin{aligned} & \exp\{\beta[\Delta + (J + J')m]\} \\ & + 2r \frac{Z_{\text{vib}}^{\text{LHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp(2\beta J_{AB}) \cosh[\beta(J - J')n] \\ & + r^2 \frac{Z_{\text{vib}}^{\text{HHS}}}{Z_{\text{vib}}^{\text{LLS}}} \exp\{-\beta[\Delta + (J + J')m]\} \end{aligned} \right]
 \end{aligned} \tag{13}$$

where $r = g_{\text{HS}}/g_{\text{LS}}$.

The high-spin fraction n_{HS} is given by:

$$\begin{aligned}
 n_{\text{HS}} &= \frac{1}{2}(n_{\text{HS}}^{(A)} + n_{\text{HS}}^{(B)}) = \frac{1}{2} \left(1 + \frac{1}{2}(\langle \sigma_A \rangle + \langle \sigma_B \rangle) \right) \\
 &= \frac{\left[r Z_{\text{vib}}^{\text{LHS}} \exp(2\beta J_{AB}) \cosh[\beta(J - J')n] \right. \\
 &\quad \left. + r^2 Z_{\text{vib}}^{\text{HHS}} \exp\{-\beta[\Delta + (J + J')m]\} \right]}{\left[Z_{\text{vib}}^{\text{LLS}} \exp\{\beta[\Delta + (J + J')m]\} \right. \\
 &\quad \left. + 2r Z_{\text{vib}}^{\text{LHS}} \exp(2\beta J_{AB}) \cosh[\beta(J - J')n] \right. \\
 &\quad \left. + r^2 Z_{\text{vib}}^{\text{HHS}} \exp\{-\beta[\Delta + (J + J')m]\} \right]} \quad (14)
 \end{aligned}$$

if we exclude vibrations, this quantity becomes:

$$\begin{aligned}
 n_{\text{HS}} &= \frac{\left[r \exp(2\beta J_{AB}) \cosh[\beta(J - J')n] \right. \\
 &\quad \left. + r^2 \exp\{-\beta[\Delta + (J + J')m]\} \right]}{\left[\exp\{\beta[\Delta + (J + J')m]\} \right. \\
 &\quad \left. + 2r \exp(2\beta J_{AB}) \cosh[\beta(J - J')n] \right. \\
 &\quad \left. + r^2 \exp\{-\beta[\Delta + (J + J')m]\} \right]} \quad (15)
 \end{aligned}$$

It is the expression of n_{HS} in the model without vibrations [6].

3. Application

3.1. Binuclear compound $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$

The binuclear compound $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$ has been a subject of several experimental studies [14] accompanied by some theoretical approaches [16] to explain the obtained results. Here, we use the present model, within some considerations on the vibration frequencies which will be mentioned later, to obtain the variation of the fraction of high-spin state n_{HS} as function of temperature (Fig. 1).

The parameters of the model exposed above are taken from the experimental values used to describe the n_{HS} with models without vibrational degrees of freedom [6]. We consider that all the modes of vibrations for molecules in a given spin state are characterized by only one effective mean frequency. This is a common and sufficient approximation [23, 24] to describe spin-crossover phenomena in configurational diagram, which leads to the presence of only three frequencies in the approach, namely ω_{LLS} , ω_{LHS} and ω_{HHS} .

Note that we have taking ($g_{\text{HS}} = 5$, $g_{\text{LS}} = 1$) because the total spin of the ion Fe^{+2} in HS state is $S = 2$; hence, the (electronic) degeneracy of this state is $g_{\text{HS}} = 5$, and for LS state, we have $S = 0$ and its degeneracy $g_{\text{LS}} = 1$. Also, we have the number of vibratory modes $p = 15$, and it is that of a transition metal ion in an octahedral environment [25].

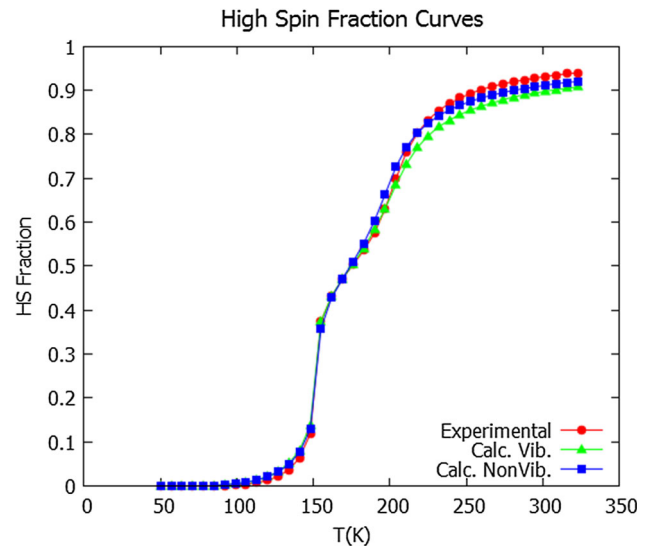


Fig. 1 Curves of the fraction n_{HS} : experimental, adjusted without vibrations ($\Delta = 778$, $J = -283$, $J' = 0$, $J_{AB} = 122$, $r = 84$) (Calc. Nonvib.) from [16] and with vibrations (Calc. Vib.) ($\Delta = 778$, $J = -283$, $J' = 0$, $J_{AB} = 122$, $g_{\text{HS}} = 5$, $g_{\text{LS}} = 1$, $\omega_{\text{LLS}} = 95$, $\omega_{\text{LLS}}/\omega_{\text{LHS}} = 1.151$, $\omega_{\text{LLS}}/\omega_{\text{HHS}} = 1.339$, $p = 15$) for the binuclear compound $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$

3.2. Effects of intramolecular vibrations

on the equilibrium temperature and the shape of the transition steps

By definition, the equilibrium temperature T_{eq} is corresponding to the $T_{\text{eq}}(n_{\text{HS}} = 1/2)$, so we have:

$$\begin{aligned}
 2 \times &\left[\frac{r Z_{\text{vib}}^{\text{LHS}} \exp(2\beta_{\text{eq}} J_{AB}) \cosh[\beta_{\text{eq}}(J - J')n]}{+ r^2 Z_{\text{vib}}^{\text{HHS}} \exp\{-\beta_{\text{eq}}[\Delta + (J + J')m]\}} \right] \\
 &= \left[\frac{Z_{\text{vib}}^{\text{LLS}} \exp\{\beta_{\text{eq}}[\Delta + (J + J')m]\}}{+ 2r Z_{\text{vib}}^{\text{LHS}} \exp(2\beta_{\text{eq}} J_{AB}) \cosh[\beta_{\text{eq}}(J - J')n]} \right. \\
 &\quad \left. + r^2 Z_{\text{vib}}^{\text{HHS}} \exp\{-\beta_{\text{eq}}[\Delta + (J + J')m]\} \right] \quad (16)
 \end{aligned}$$

But the condition $n_{\text{HS}}(T_{\text{eq}}) = \frac{1}{2}$ means $m(T_{\text{eq}}) = (\langle \sigma_A \rangle + \langle \sigma_B \rangle) = 0$, so we obtain:

$$\exp\{2\beta_{\text{eq}}\Delta\} = r^2 \frac{Z_{\text{vib}}^{\text{HHS}}}{Z_{\text{vib}}^{\text{LLS}}} = \left((g_{\text{HS}}/g_{\text{LS}}) \sqrt{Z_{\text{vib}}^{\text{HHS}}/Z_{\text{vib}}^{\text{LLS}}} \right)^2 \quad (17)$$

Finally, we have:

$$T_{\text{eq}} = \Delta / \left[k_B \ln \left((g_{\text{HS}}/g_{\text{LS}}) \sqrt{Z_{\text{vib}}^{\text{HHS}}/Z_{\text{vib}}^{\text{LLS}}} \right) \right] \quad (18)$$

which becomes, in the approximation of high temperatures–low frequencies ($k_B T_{\text{eq}} \gg \hbar\omega_{\text{LLS}}^{(i)}$):

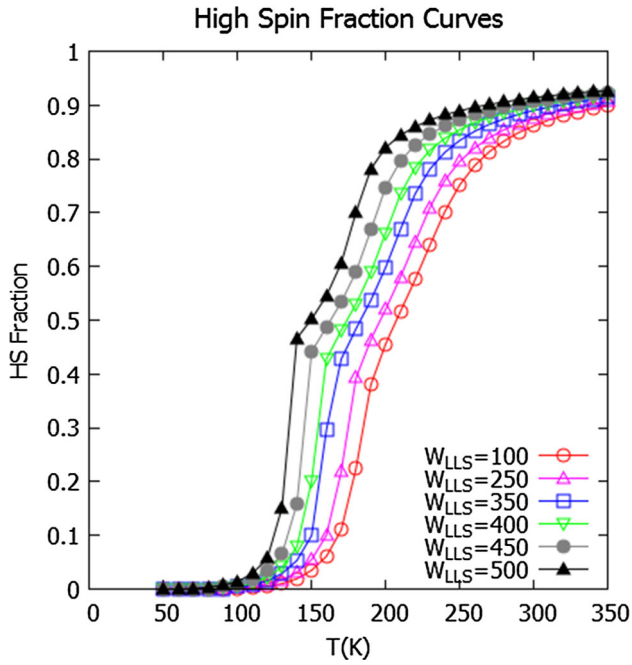


Fig. 2 Curves of the fraction n_{HS} calculated in the framework of the electro-vibrational model with the values of the frequency ω_{LLS} shown in the figure, and with:

$$\left(\begin{array}{l} \Delta = 778, J = -283, J' = 0, J_{AB} = 122, g_{\text{HS}} = 5, \\ g_{\text{LS}} = 1, \omega_{\text{LLS}}/\omega_{\text{LHS}} = 1.151, \omega_{\text{LLS}}/\omega_{\text{HHS}} = 1.339, p = 15 \end{array} \right)$$

$$T_{\text{eq}} = \Delta / \left[k_B \ln \left(\left(g_{\text{HS}}/g_{\text{LS}} \right) \prod_{i=1}^p \sqrt{\omega_{\text{LLS}}^{(i)} / \omega_{\text{HHS}}^{(i)}} \right) \right] \quad (19)$$

We notice that the T_{eq} is independent of the frequency of the intermediate state (LS–HS or HS–LS) ω_{LHS} , as mentioned by Real et al. [14]. Within the same approximation ($k_B T_{\text{eq}} \gg \hbar \omega_{\text{LLS}}^{(i)}$), the equilibrium temperature is a function of $\sqrt{\omega_{\text{LLS}}/\omega_{\text{HHS}}}$ for binuclear molecules, whereas in mononuclear molecules, it is a function of $\omega_{\text{LS}}/\omega_{\text{HS}}$ [18].

In addition, our model aims to reproduce the two-step spin transition curves observed in some binuclear molecules (Fig. 1) and we demonstrate the effects of the intramolecular vibrations on the shape of these spin transition steps as shown in Fig. 2.

In the following, we have set the parameters of the model Δ, J, J' and J_{AB} to the values of the adjustment of the experimental curve $n_{\text{HS}}(T)$ of the compound $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpy}$.

The calculated fractions of molecules in HS, $n_{\text{HS}}(T)$, for several values of the frequency ω_{LLS} and for some values of frequency ratios $\omega_{\text{LLS}}/\omega_{\text{LHS}}$ and $\omega_{\text{LLS}}/\omega_{\text{HHS}}$ are presented in (Fig. 2).

For the values of $\omega_{\text{LLS}}/\omega_{\text{LHS}}$ and $\omega_{\text{LLS}}/\omega_{\text{HHS}}$ fixed to those of the adjusted curve, and for the large values of the

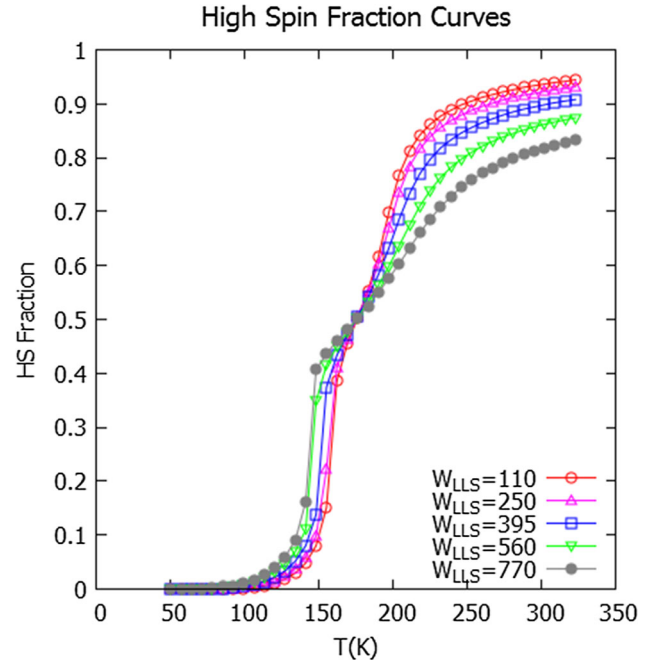


Fig. 3 Curves of the fraction n_{HS} calculated in the framework of the electro-vibrational model with the values of the frequency ω_{LLS} shown in the figure, and for: ($\omega_{\text{LLS}}/\omega_{\text{LHS}} = 1.201, 1.18, 1.151, 1.12, 1.091$), respectively, and for: ($\Delta = 778, J = -283, J' = 0, J_{AB} = 122, g_{\text{HS}} = 5, g_{\text{LS}} = 1, \omega_{\text{LLS}}/\omega_{\text{HHS}} = 1.339, p = 15$)

frequency ω_{LLS} , the two-step plateau of the transition curves manifests clearly and the equilibrium temperature T_{eq} moves to the lower temperatures (Fig. 2). This is due to the fact that the increase in ω_{LLS} with fixed ratios $\omega_{\text{LLS}}/\omega_{\text{LHS}}$ and $\omega_{\text{LLS}}/\omega_{\text{HHS}}$ leads to a smaller increase in the frequencies ω_{LHS} and ω_{HHS} . This reduces the vibrational energy gap between the phases (HS–HS), (LS–HS) and (LS–LS) and leads to an increase in the separation between the vibrational energy levels in the same spin phase. Consequently, the population of the states in the phases (HS–HS) and (LS–HS) shifted to low temperatures and leads to smoother curves for the phases with high density of vibrational states, i.e., the phases (HS–LS) and (HS–HS) with energy levels of electronic degeneracy $g_{\text{HS}}g_{\text{LS}}$ and g_{HS}^2 , respectively.

On the other hand, when we also vary the ratio $\omega_{\text{LLS}}/\omega_{\text{LHS}}$, and for a selective choice of values of this ratio, we can find all curves of the fraction $n_{\text{HS}}(T)$ interfering in one point; it is the equilibrium temperature ($T_{\text{eq}} \approx 175.5$ K). In addition to this, for the great values of ω_{LLS} , the first step of the transition curves ($T < T_{\text{eq}}$) becomes more steeper, while the second one ($T > T_{\text{eq}}$) is less abrupt, and this is more obvious for the smaller values of $\omega_{\text{LLS}}/\omega_{\text{LHS}}$, where ω_{LHS} values are in the order of that

of ω_{LLS} . This leads to a degeneracy of vibrational states associated with higher energy levels separations. This increases the population of these states for wide temperature range around the equilibrium temperature, which translated in second-step smoother (Fig. 3).

4. Conclusion

In this paper, we have revised and then applied the electrovibrational Ising-type model for binuclear spin-crossover molecules such as $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$ compound.

The curve of the transition is well reproduced. We showed that for the binuclear spin-crossover molecules, the ratio of $n_{\text{HS}}(T)$, in the approximation of high temperatures–low frequencies, is proportional to $\sqrt{\omega_{LLS}/\omega_{\text{HHS}}}$ instead of $\omega_{\text{LS}}/\omega_{\text{HS}}$ for mononuclear molecules. We did also produce the plateau observed in binuclear spin-crossover curves and showed that the equilibrium temperature T_{eq} moves to the lower temperatures as function of ω_{LLS} and that all curves pass by a common point corresponding to T_{eq} .

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