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Nanomaterials and their physical properties

The spin-crossover phenomenon: towards molecular memories

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Abstract

We describe some of our principal results on the thermo- piezo- and magneto-switching of spin crossover phenomenon in inorganic molecular materials: experimental properties, theoretical approaches and channels for molecular memory devices. ***To cite this article: A. Bousseksou, G. Molnar, C. R. Chimie 6 (2003).***

Keywords: spin crossover; hysteresis loop; pressure; magnetic field; dielectric constant

1. Introduction

Pseudo-octahedral iron (II) complexes displaying spin crossover between the $^1A_1$ low-spin (LS) and the $^5T_2$ high-spin (HS) states have been the subject of much work during the last decades [1]. The spin state of the central metal ion can be altered under external perturbations, such as temperature, pressure, light or magnetic fields [2, 3]. These spin-crossover complexes, displaying thermo-, photo-, piezo-and magneto-chromic properties, are of growing importance in the area of functional materials research, especially for application in memory and display devices and as molecular switches [3]. Beside fundamental research, there have been several proposals for the design of information processing devices (e.g. memories, displays, etc.) based on SCO spin crossover compounds. For example, the discovery of the LIESST (light induced excited state spin trapping) effect suggested that the SCO complexes could be used as optical switches. In fact, it is important to notice that the LIESST effect is a monomolecular process, leading to the very exciting idea of high-density information storage. For the moment the highest temperature value where the LIESST is observed is around 130 K. The main question remaining concerning the chemical synthesis efforts is finding the ways for increasing the temperature where this effect occurs. Another interesting approach to build memory devices from SCO materials is based on the fact that the thermal spin transition may occur with hysteresis loop, conferring a memory effect to these systems ([1] and references therein). Indeed, inside the temperature range of the hysteresis loop, the spin state of the system depends on its history, hence on the information that has been stored. Since the optical and magnetic properties of the material are markedly different in the two spin-states this information can be read easily by optical or magnetic means. Of course, the ideal situation is when the hysteresis cycle is centered on room temperature. The first spin-crossover complex with large and abrupt

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thermal hysteresis loop around room temperature was reported in 1993 in conjunction with optical reading and thermal addressing of the stored information [4]. This report has been followed by an intense research for compounds with hysteresis at room temperature, and today several examples are known. Besides thermal addressing of spin crossover materials, we reported very recently switching of spin states by short magnetic field [2,3] or a pulse of pressure in the thermal hysteresis interval [5]. And more recently we evidenced hysteresis loops in dielectric constant of spin crossover compounds with first order spin transitions [6]. In this paper we report a brief summary of our most important results obtained on the thermo-, magneto- and piezo-switching of the spin crossover phenomenon.

2. Discovery of a hysteresis loop in the dielectric constant in spin crossover phenomenon complexes: toward molecular memory devices (after [6,7])

Very recently we discovered the possibility to observe a hysteresis loop in the dielectric constant of the spin crossover complexes [6]. This discovery is considered as a break-through for the use of the spin crossover systems and opens many interesting potentialities in a context where the molecular level is being considered as the answer of the miniaturization. In fact as shown in Fig. 1, the thermally induced spin crossover around room temperature in $[Fe(NH_2trz)_3](NO_3)_2$ is well observed in the temperature dependence of the dielectric constant. This complex exhibits a wide (50 K) dielectric hysteresis loop around room temperature (Fig. 1a), in agreement with the magnetic susceptibility measurements (Fig. 1b). This first observation of a hysteretic bistability in dielectric properties of spin crossover compounds opens a new way to read out information. The dielectric hysteresis property is actually the first effective means allowing the use of spin crossover materials in electronic devices, leading to high-density information storage, i.e., re-inscribable memory with molecular materials. Thin micro, nano-films of this material have been deposited on an adequate substrate by using the standard techniques of microelectronics [7]. The hysteresis loop of the film's dielectric constant has been confirmed leading to the first effective component for electronics, which is, already, patented [7].

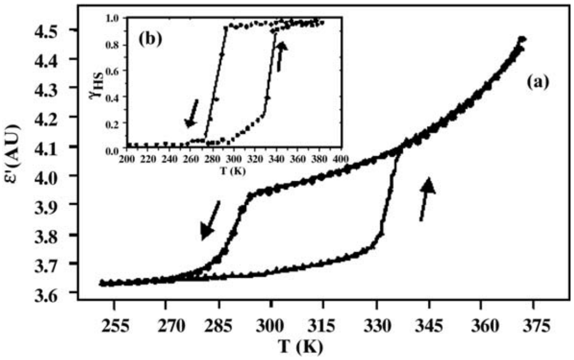

Fig. 1. **(a)** Thermal hysteresis of the dielectric constant associated with the spin-transition of $[Fe(NH_2trz)_3](NO_3)_2$. **(b)** Thermal variation of the proportion of high-spin molecules (γ_{HS}) in $[Fe(NH_2trz)_3](NO_3)_2$ obtained through magnetic susceptibility measurements. Data points are connected to guide the eye (after [6]).

3. The magneto-switching of the spin crossover (after [2,3])

It is well known that the application of a magnetic field stabilizes the high-spin (HS) state over the low-spin (LS) state and therefore shifts the thermal spin-crossover to lower temperatures. Sasaki and Kambara using ligand field calculation ([3] and references therein) predicted this effect and its magnitude. The first experimental study using a static magnetic field of 5.5 T was reported by Gütlich laboratory (Mainz, Germany). They observed a –0.1 ± 0.04 K shift of the transition temperature ($T_{1/2}$) for the complex $[Fe(phen)_2(NCS)_2]$. Three other studies have been reported later with Co^{III}, Fe^{II} and Mn^{III} central ions ([3] and references therein) under somewhat higher static fields (10–23 T). In all cases, small shifts in $T_{1/2}$ (from –0.1 to –1.6 K) were detected. Very recently, we have reported the effect of a *pulsed* magnetic field on the spin-crossover systems $[Fe(phen)_2(NCS)_2]$ [2], $Fe_xNi_{1-x}(btr)_2(NCS)_2 \cdot H_2O$ (with $x = 0.33$, 0.52 or 0.8) [8,9] and $[Co(H_2(fsa)_2en)]py_2$ [3]. The principal results for $Fe(phen)_2(NCS)_2$ and $[Co(H_2(fsa)_2en)]py_2$ are shown in Figs. 2 and 4, respectively. The main findings can be summarised as follows:

(*i*) As shown in Fig. 2, applying a 1-s pulsed 32-T magnetic field to the spin transition solid Fe $(phen)_2(NCS)_2$, sizeable effects are observed on the high-spin fraction. In the hysteresis loop tem-

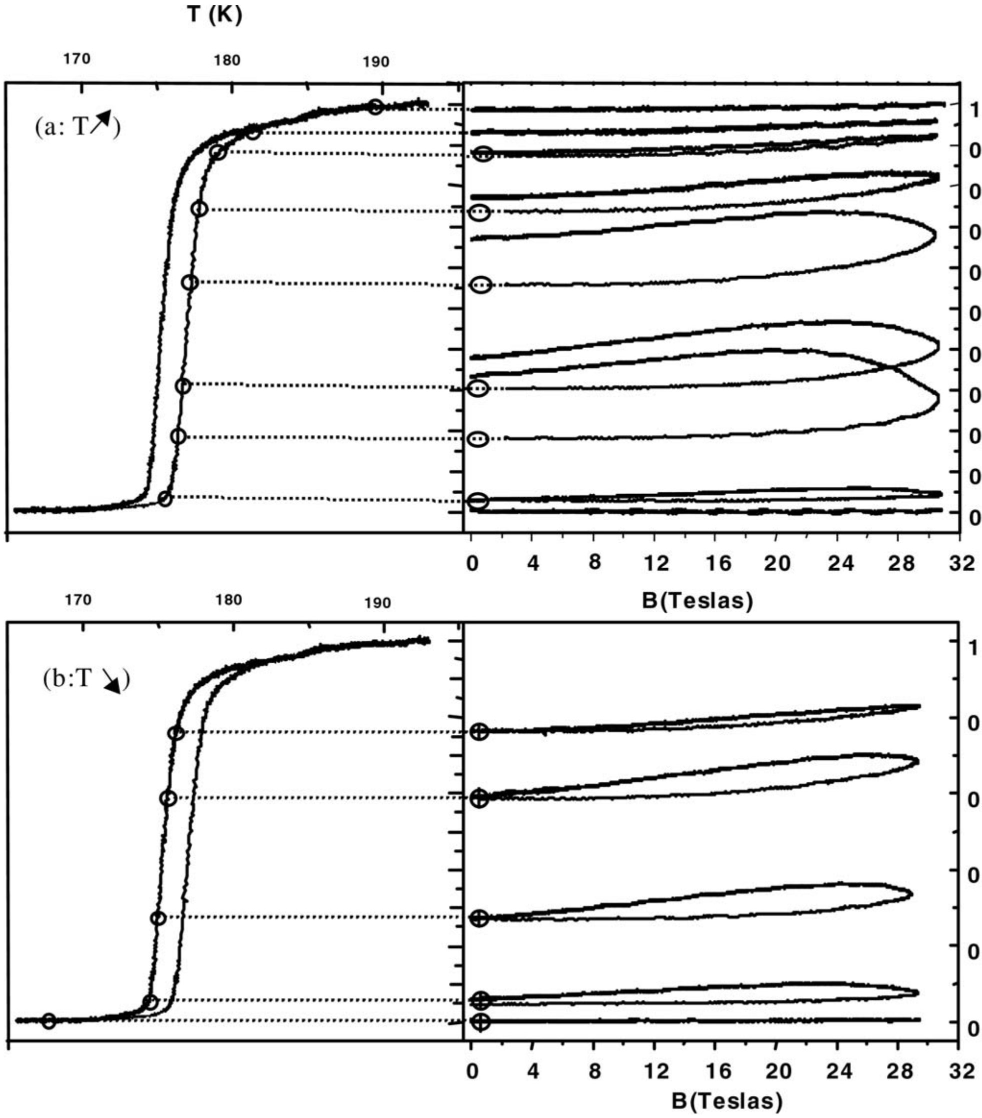

Fig. 2. $Fe(phen)_2(NCS)_2$, the complete set of pulsed field experiments in the ascending (**a**) and descending (**b**) branches of the thermal hysteresis loop. Open circles show initial states (after [2]). n_{HS} is the proportion of high-spin molecules.

perature range, an increase of 15% in the HS fraction is obtained, with an irreversible (reversible) character in the ascending (descending) branch of the loop [2]. The time dependence of the HS fraction provides information on the kinetics of the spin-crossover process at the spin transition. As shown in Fig. 3, delays between the excitation (magnetic field) and the response (increase of the high-spin proportion) have been observed: 90 ms (50 ms) in the ascending (descending) branch.

(*ii*) Applying a pulsed magnetic field of 32 T to the solid $Co^{II}(H_2(fsa)_2en)py_2$ (Fig. 4) led for the first time to an irreversible and quasi-complete triggering $S = 1/2 \rightarrow S = 3/2$ [3].

(*iii*) A correlation between the delay (excitation/response) and the cooperativity of the spin-crossover phenomenon has been evidenced by

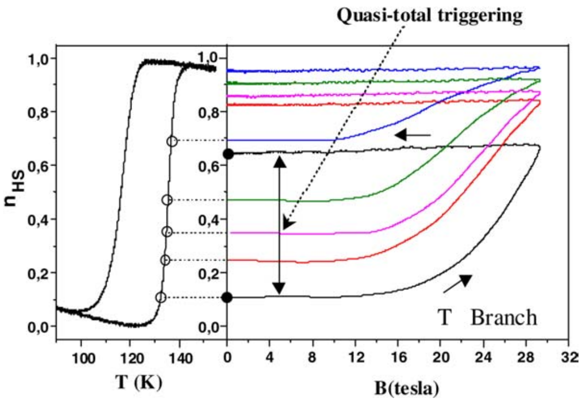

Fig. 4. Set of isotherms $n_{HS}(T,B)$ showing the irreversible (and quasi-total) triggering effect on the HS fraction in $Co(H_2(fsa)_2en)(py)_2$ for an applied pulsed magnetic field in the metastable LS state (after [3]).

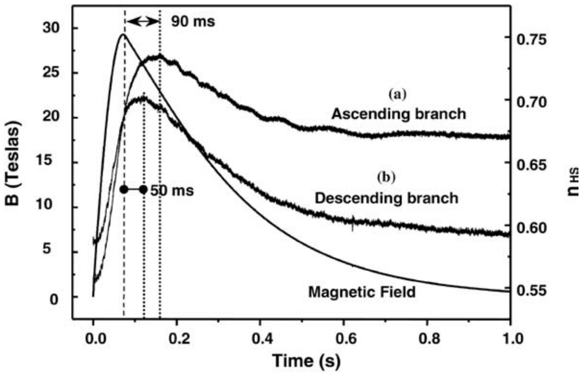

Fig. 3. $Fe(phen)_2(NCS)_2$, the time dependencies of two typical responses $n_{HS}(t)$, for initial states belonging to the ascending (**a**) and descending (**b**) branches of the thermal hysteresis loop. For comparison, the time dependence of the magnetic-field pulse is also shown (after [2]).

studying the effect of pulsed magnetic field on the family of diluted complexes $[Fe_xNi_{(1-x)}(btr)_2(NCS)_2]\cdot H_2O$ [8,9] where the dilution x controls the cooperativity. An exponential dependence between the delay (excitation/response) and the cooperativity has been evidenced [9].

4. The piezo-switching of the spin crossover (after [5,10])

Since the beginning of spin-crossover research, several authors have discussed the interest of pressure experiments for spin-crossover systems. We briefly recall that pressure favours the low spin state, due to its smaller volume, and therefore shifts the spin transition towards higher temperatures, or speeds up the relaxation back to the low spin state at a given temperature. Even if pressure ranks with temperature as a useful thermodynamic parameter, it is much less explored owing to the difficulties of working under high, hydrostatic pressure and low temperature at the same time. For this reason, we have recently undertaken – in collaboration with the LMOV (F. Varret's laboratory, Versailles, France) and the QUB [J.J. Mc-Garvey's laboratory, Belfast, NI) – the development of a high-pressure/low-temperature system that can be coupled to different optical (sapphire window) and Mössbauer (B_4C window) spectrometers as well. At the present time, our system allows attainment of 2 kbar pressure using cold helium gas or liquids as pressure-transmitting medium. Using these equipments, interesting piezo-chromic properties have been observed on different spin-crossover complexes by Raman spectroscopy for the first time [10]. The spin state of a series of cyanide-bridged, iron(II) spin-crossover coordination polymers of formula $Fe(pyrazine)[M(CN)_4]\cdot 2H_2O$ (M = Ni, Pd or Pt) have been studied by recording their solid state Raman spectra at room temperature as a function of pressure (Fig. 5). For the first time, a reproducible piezo-hysteresis loop has been observed at room temperature for the Ni complex with characteristic spin transition pressures of $P_{1/2}\uparrow$ = 1350 bar

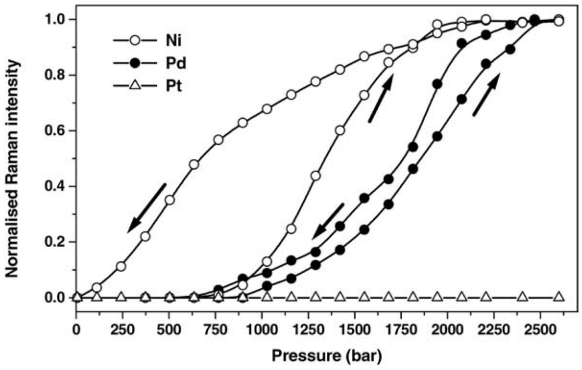

Fig. 5. Intensity of the 675-cm^{-1} LS marker band as a function of pressure for the complexes $Fe(pz)[M(CN)_4]\cdot 2H_2O$ (M = Ni, Pd or Pt) at room temperature. Arrows indicate the increase and subsequent decrease of the pressure (after [10]).

and $P_{1/2}\downarrow$ = 650 bar (Fig. 5). The fascinating feature here is the use of a perturbation other than the temperature to obtain a memory effect! For the Pd and Pt complexes, the spin-state change occurs at higher pressures and competes with a pressure-induced structural transformation. This investigation is the first time that high-pressure Raman spectroscopy has been used to follow the pressure induced spin-state change in SCO complexes. This method has also been used in conjunction of diamond anvil cell technique and we could observe a spin state change for the complex Fe(pyridine)$_2$[Ni(CN)$_4$] at around 10 kbar.

Beside the static effects of pressure on the spin transition, we have also studied the effects of a pressure pulse in the temperature range of the thermal hysteresis loop for the compound Fe(phen)$_2$(NCS)$_2$. In this compound, the pressure was found to upward shift the spin-transition temperature by 23 K kbar^{-1}. During the dynamic pressure pulse, a decrease in n_{HS} is observed, with an irreversible (reversible) character in the *descending* (ascending) branch of the hysteresis loop. In this respect, pressure has a ‘mirror effect’ compared to the application of an intense and pulsed magnetic field, for which -as we reported recently [5] – an increase in n_{HS} is observed, with an irreversible (reversible) character in the ascending (descending) branch of the hysteresis loop. While an applied magnetic field stabilizes the HS state via the Zeeman effect, external pressure stabilizes the LS state due to the work term. Therefore, a pressure (magnetic) pulse results in an irreversible decrease (increase) of n_{HS} in the descending (ascending) branch of the thermal hysteresis cycle, whereas these changes are always reversible in the ascending (descending) branch (Figs. 2,4,6). If one compares the theoretical shift of the transition temperature under quasi-static external pressure and magnetic field, it appears that, in the case of Fe(phen)$_2$(NCS)$_2$, the effect of 1 T is roughly the opposite of the shift caused by 2.5 bar! The fact that such small pressure as 200 bar triggered a complete crossover between the two spin-states suggests that piezo effects might be implemented in devices for addressing SCO materials. Of course, similar studies are in progress, with the well known compounds with T_c at room temperature, in order to select those who have the same response to a pulse of pressure than Fe(phen)$_2$(NCS)$_2$. More detailed analysis is given by Varret et al. [11].

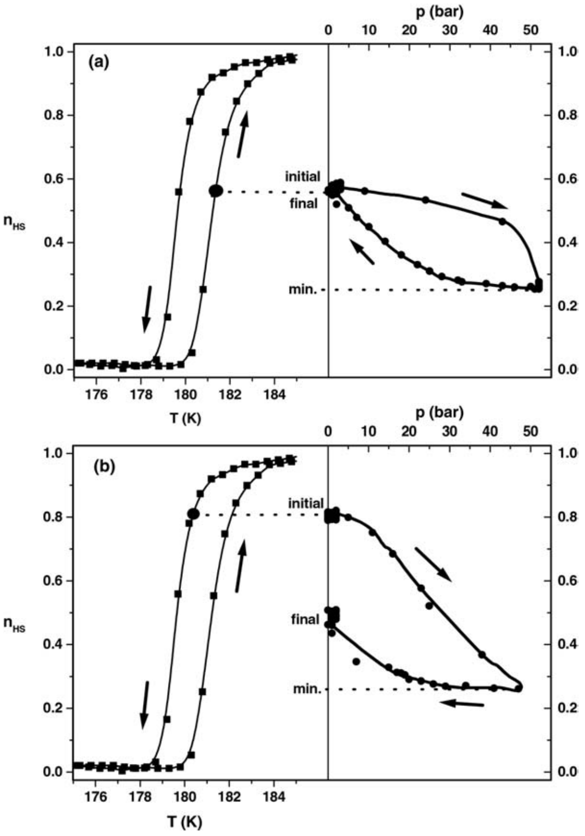

Fig. 6. Pressure effect on the high spin fraction $n_{\mathrm{HS}}(T,p)$ in Fe(phen)$_2$(NCS)$_2$ showing (**a**) a reversible triggering in the ascending branch and (**b**) an irreversible triggering in the descending branch of the thermal hysteresis loop in contrast of the effect of magnetic field (after [5]).

5. Theoretical models

5.1. Two level Ising-like model (after [12,13] and references therein)

To describe a system with two energy levels, a fictitious spin $\hat{\sigma}$ is associated with the HS and LS states for each molecule i. The Hamiltonian of the system is expressed as a function of the energy gap Δ_0 between the two levels of an isolated molecule and a phenomenological parameter J_{ij}, describing the interactions between the molecules i and j: $\hat{\mathbf{H}}_i = \frac{\Delta_0}{2}\hat{\sigma}_i + \sum_{j\neq i} J_{ij}\hat{\sigma}_i\hat{\sigma}_j$ (1), where $\hat{\sigma}$ is a fictitious spin operator with eigenvalues +1 or –1 for the HS and LS states, respectively. Each level in this model represents an effective level including the electronic configuration and the vibrational density of states.

5.2. The mean-field approximation (after [12] and references therein)

In order to solve analytically the Hamiltonian (1), we use the mean-field approximation where the interaction-energy of the neighbouring molecules is averaged as $J\langle\hat{\sigma}\rangle$: $\sum_{j\neq i} J_{ij}\,\hat{\sigma}_i\,\hat{\sigma}_j \to J\langle\hat{\sigma}\rangle\hat{\sigma}_i$. Using this approximation, we can deduce the high-spin fraction n_{HS} through the average of the fictitious spin $\langle\hat{\sigma}\rangle$: $n_{HS} = \dfrac{\langle\hat{\sigma}\rangle + 1}{2}$, as well as the transition temperature ($T_{1/2}$), defined as the temperature for which the proportions of LS and HS molecules are equal (n_{HS} = n_{LS} = 1/2). By determining the mean value $<\hat{\sigma}>$, we obtain the thermal variation of the proportion of high-spin molecules: $n_{HS}(T) = \dfrac{r}{r + \exp\dfrac{\Delta_0 - 2J(2n_{HS} - 1)}{k_{\mathrm{B}}T}}$,

with $r = \dfrac{g_{\mathrm{HS,vib}}}{g_{\mathrm{LS,vib}}}$ with the degeneracies ratio of the high-spin and low-spin levels respectively, including the vibrational contributions, and $T_{1/2} = \dfrac{\Delta_0}{k_{\mathrm{B}}\ln\left\{\dfrac{g_{\mathrm{HS,vib}}}{g_{\mathrm{LS,vib}}}\right\}}$.

In the case where $J > T_{1/2}$, one obtain a discontinuity of the first derivative of the free energy F of the system leading to a first order spin transition. We observe in this case a hysteresis loop. This model reproduces the main thermal spin-crossover behaviours observed experimentally as shown in Fig. 7 and as reported in [14] for the two-step spin crossover systems.

5.3. Introduction of the molecular vibrations (after [15,16])

In the case of ferrous SCO compounds, the increase in antibonding e_g electrons upon a $\mathrm{LS}(t_{2g}^{\,6}) \to \mathrm{HS}(t_{2g}^{\,4}e_g^{\,2})$ transition significantly weakens the metal–ligand bonds. Thus, the vibrational modes are necessarily affected by the change in spin-state are the metal-ligand stretching and bending frequencies. We studied thus the effect of intramolecular vibrations on the SCO of independent molecules involving a set of harmonic oscillators [15]. Each two-level molecule is associated with p harmonic oscillators having two possible frequencies, ω_{LS} and ω_{HS}. For each oscillator, of frequency ω_i, the vibrational partition function is written:

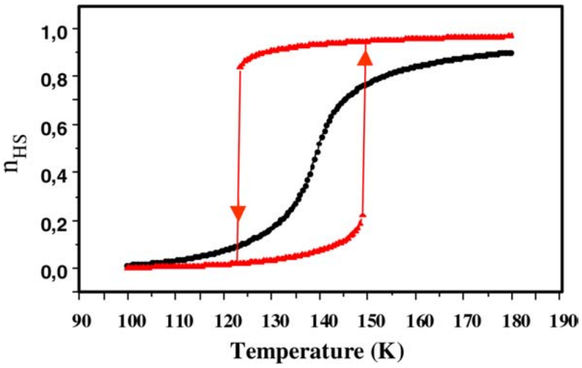

Fig. 7. Typical thermal variation of the proportion of high-spin molecules $n_{\mathrm{HS}}(T)$ obtained by the Ising-like model: gradual spin crossover ($J < T_{1/2}$: black curve); abrupt spin crossover with hysteresis loop ($J > T_{1/2}$: red curve).

$$z_i(\omega_i, T) = 1/[\exp(\hbar\omega_i/kT) - 1]$$

The contribution of each oscillator (i) to the total entropy is then derived from the free energy expression ($F_i = -k\,T\ln z_i$; $S_i = -\partial F_i/\partial T$), leading to:

$$S_i(\omega_i, T) = \hbar\omega_i/2T\tanh(\hbar\omega_i/2kT) - k\ln[2\sinh(\hbar\omega_i/2kT)]$$

The total entropy of the system is calculated by summing up the contributions of the considered vibrational modes [17, 18]. The decrease in frequencies upon LS→HS crossover results in an entropy increase, expressed by: $\Delta S(T) = S_{\mathrm{HS}}(T) - S_{\mathrm{LS}}(T)$.

The different steps of the theoretical approaches using the Ising-like theoretical method are shown in Fig. 8. An interesting situation is obtained due to the intramolecular vibrations contributions: the system may be in a critical situation. In fact, this situation corresponds to the case where $\Delta_{\mathrm{eff}} = \Delta_{\mathrm{elec}} - p\,\hbar\,(\omega_{\mathrm{LS}} - \omega_{\mathrm{HS}})\,/\,2 \sim 0$, i.e. – in the case where the contribution of the vibrations is of the same order of magnitude as the electronic gap between the HS and LS states – the high-spin and low-spin states are equi-energetic. The high-spin state may be the ground state at low temperatures and one may observe a very partial HS → LS → HS spin crossover phenomenon [15]. This is illustrated in Fig. 9. This equi-energetic situation has been experimentally observed by Mössbauer spectroscopy for the first time in [16].

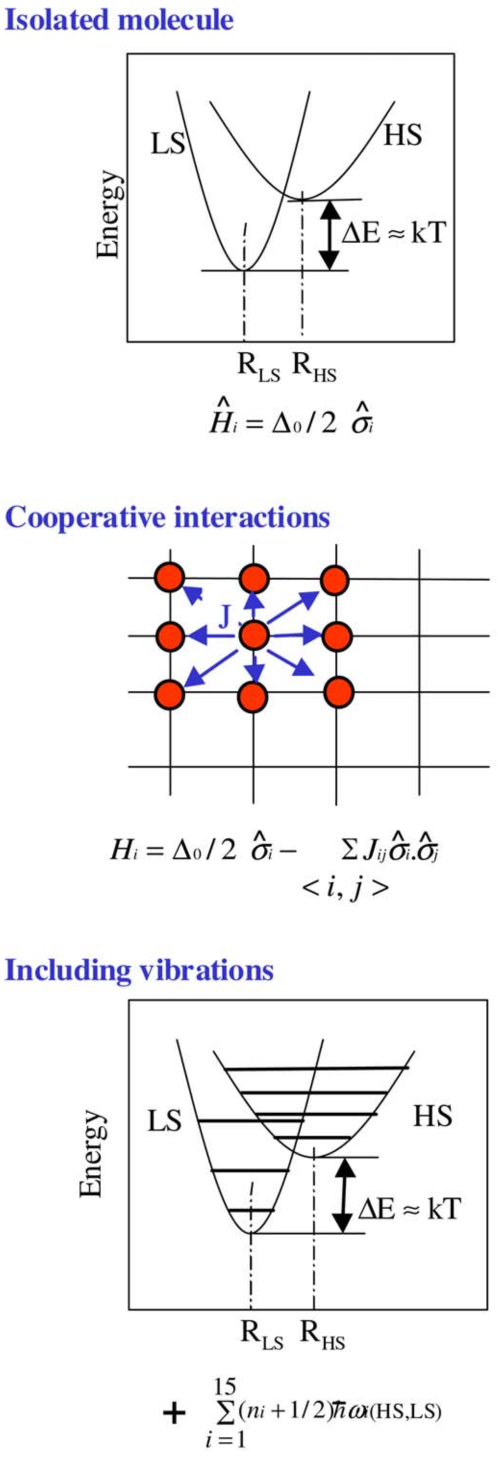

Fig. 8. Theoretical steps of the Ising-like model approach for spin-crossover phenomenon.

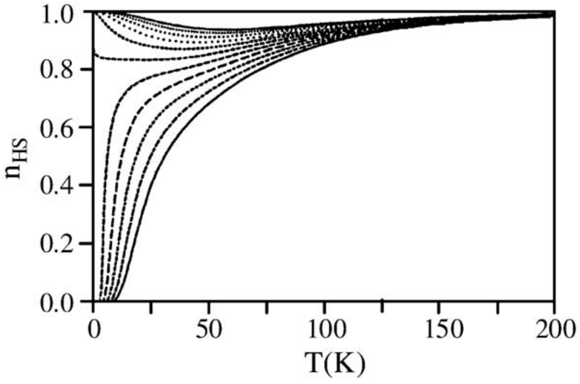

Fig. 9. Theoretical thermal variation of the proportion of high molecules in the equi-energetic high spin low spin critical situation $\Delta_{\mathrm{eff}} = \Delta_{\mathrm{elec}} - p\,\hbar(\omega_{\mathrm{LS}} - \omega_{\mathrm{HS}})/2 \sim 0$,after [15]).

5.4. Introduction of the magnetic field (after [3,19,20])

The magnetic field, via the Zeeman effect, removes the electronic degeneracies of the HS and LS levels, and the new Hamiltonian is written as:

$$\hat{\mathbf{H}}_i(m_S) = \frac{\Delta_0}{2}\hat{\sigma}_i + \sum_{j \neq i} J_{ij}\hat{\sigma}_i\hat{\sigma}_j + g_{\mathrm{L}}\mu_{\mathrm{B}} B \hat{S}_Z \frac{\hat{\sigma}_i + 1}{2}$$

where μ_{B} is the Bohr magneton, g_{L} is the Landé factor, B is the magnetic field strength and S_Z is the projection of the spin moment operator along the field direction. This latter can take any of the $2S+1$ values $m_S = -S, -S+1, ..., S$. The system is described now by its spin state $\hat{\sigma}_i$ and also by m_S. By using the mean-field approximation the proportion of high-spin molecules n_{HS} as function of temperature and magnetic field is written as:

$$n_{\mathrm{HS}}(B,T) = \frac{r(B)}{r(B) + \exp\dfrac{\Delta_0 - 2J(2n_{\mathrm{HS}} - 1)}{k_{\mathrm{B}}T}}$$

with $r(B) = \dfrac{g_{\mathrm{HS,vib}}\, g(B, S_{\mathrm{HS}})}{g_{\mathrm{LS,vib}}\, g(B, S_{\mathrm{LS}})}$

and $g(B,S) = \dfrac{\sinh\left(\dfrac{(2S+1)g_{\mathrm{L}}\mu_{\mathrm{B}}B}{2k_{\mathrm{B}}T}\right)}{\sinh\left(\dfrac{g_{\mathrm{L}}\mu_{\mathrm{B}}B}{2k_{\mathrm{B}}T}\right)}$

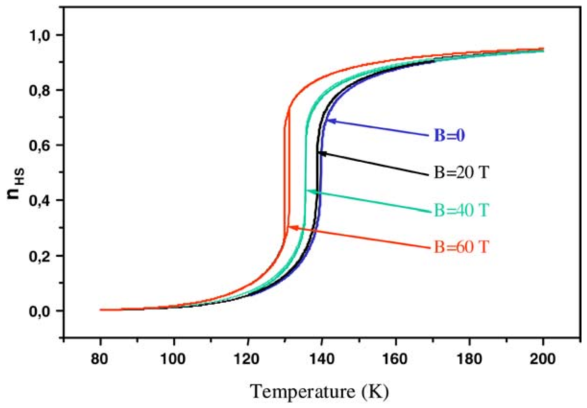

Fig. 10. Calculated thermal variation of the proportion of high spin molecules under static magnetic $n_{\mathrm{HS}}(T,B)$ field by using the Ising-like model (after [21]).

and for $T_{1/2}$:

$$T_{1/2}(B) = \frac{\Delta_0}{k_B \ln\left\{ \frac{g_{\mathrm{HS,vib}}}{g_{\mathrm{LS,vib}}} \cdot \frac{\sinh\left[\frac{(2S_{\mathrm{HS}}+1)g_L \mu_B B}{2k_B T_{1/2}}\right]}{\sinh\left[\frac{(2S_{\mathrm{LS}}+1)g_L \mu_B B}{2k_B T_{1/2}}\right]} \right\}}$$

The exact solution of the self-consistent $n_{\mathrm{HS}}(T,B)$ can be obtained only numerically! Fig. 10 represents the resolution of equation $n_{\mathrm{HS}}(T,B)$, for each fixed temperature, using the Newton numerical method. This resolution was carried out in the case of a gradual conversion between the diamagnetic ($S_{\mathrm{LS}} = 0$) and the paramagnetic ($S_{\mathrm{HS}} = 2$) spin states with the parameter set $\Delta_0 = 700$ K, $J = -139$ K, $g_{\mathrm{HS,vib}}/g_{\mathrm{LS,vib}} = 30$, for different strengths of the applied magnetic field. One can note that for an applied magnetic field above 40 T, a first-order phase transition appears, accompanied by a thermal hysteresis. In fact, the magnetic field decreases the transition temperature, but the condition for a first-order transition $J/k_B\ T_{1/2} > 1$ remains unchanged. As described in [19], we can also obtain an analytical expression for the variation of $T_{1/2}$ as a function of the applied magnetic field strength from the Landau free energy in presence of a field and in thermodynamic equilibrium: $\delta T_{1/2} = -\frac{4(\mu_B B)^2}{k_B \Delta_0}$, for the case $S_{\mathrm{LS}} = 0$, $S_{\mathrm{HS}} = 2$.

5.5. Monte Carlo method (after [19,21])

The mean-field approximation is not well adapted to determine the exact value of the hysteresis loop, even if this method is powerful for understanding the main ingredients of the spin-crossover phenomenon [12,13]. We have thus used, as suggested in [17], the Monte Carlo–Metropolis method to solve statistically the Hamiltonian (1). This work is described in [19]. In the case of the application of a static magnetic field for Fe (II) complexes, the equilibrium condition we used in the Monte-Carlo algorithm are:

$$g_{\mathrm{vib\ HS}} \cdot e^{-\beta E_{\mathrm{HS}_i}} \cdot W_{\mathrm{HS}_i \to \mathrm{LS}} = g_{\mathrm{vib\ LS}} \cdot e^{-\beta E_{\mathrm{LS}}} \cdot \frac{W'_{\mathrm{LS} \to \mathrm{HS}_i}}{5},$$

with $i = -2,-1,0+1,+2$, and $W_{\mathrm{LS}\to\mathrm{HS}}$ is the transition rate LS → HS. The sum of the five equations used by the algorithm confirms well the detailed balance condition [21].

5.6. Introduction of pressure (after [10,22])

To consider the effect of pressure, we replaced the gap Δ in the Ising-like model by $\Delta + P\,\Delta V$. The new Hamiltonian is thus function of temperature and pressure. The proportion of HS molecules are deducted from the calculated average $<\sigma>(T, p)$. This model reproduces very well the main experimental data under pressure ([10,22] and references therein).

6. Conclusion

Molecular spin crossover is one the most spectacular example of bistability phenomenon. Even if we have spent a lot of time and efforts (more than 15 years), and much more by other French and European pioneer teams, in this fascinating field (chemical synthesis, physical experiments and theory), we feel however that we are just starting! In fact, many important questions remain and need to be deeply studied. One can mention, for example, the study of the effect of size reduction on the dynamics of the spin crossover phenomenon and the stability of the information storage. Another important point is the study of the origin of the change in dielectric properties upon spin-crossover phenomenon, which opens a new field of research. These exciting questions will be the subject of our main efforts in the nearest future.

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