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Molecules with two electronic energy levels :  
thermal hysteresis  
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bond.

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**Abstract**

A spin-conversion molecule is organised around an iron ion  $Fe^{+2}$ . This ion has two quantum energy levels : a low spin (LS) ground level,  $S = 0$ , and a high spin (HS) excited level,  $S = 2$ , where  $S$  is the total spin of the  $3d$  electrons. A macroscopic crystal of a spin-conversion molecule has two thermodynamic phases : a diamagnetic phase where all the molecules are in (LS) level and a paramagnetic phase where they are all in (HS) level. The diamagnetic phase is stable at low temperature. For some spin-conversion crystals, the phase change is accompanied by a thermal hysteresis cycle and for some of them, this hysteresis still exists in very small nanoparticles. From what size this hysteresis can appear and which are the microscopic parameters responsible for it ?

It has been shown that a single spin-conversion molecule passes without hysteresis from one level to the other when its temperature varies. In the present theoretical study we consider the case of two spin conversion molecules linked by a chemical bound. We assume that the value of the elastic force constant of the spring between the two molecules depends on the quantum states of the molecules. A thermal hysteresis cycle can be obtained.

# 1 Introduction

A spin-conversion molecule is organised around an iron ion  $Fe^{+2}$ . This ion has two quantum energy levels : a low spin (LS) ground level,  $S = 0$ , and a high spin (HS) excited level,  $S = 2$ , where  $S$  is the total spin of the  $3d$  electrons [1]. Let us call  $\Delta$  the difference between the energies of the two levels and  $r$  the degeneracy of the excited level. This degeneracy is given by  $r = 2S + 1$ .

A macroscopic crystal of a spin-conversion molecule has two thermodynamic phases : a diamagnetic phase where all the molecules are in (LS) level and a paramagnetic phase where they are in (HS) level. The diamagnetic phase is stable at low temperature. For some spin-conversion crystals, the phase change is accompanied by a thermal hysteresis cycle [2 – 10] and for some of them, this hysteresis still exists in very small nanoparticles [11 – 17]. From what size this hysteresis can appear and which are the microscopic parameters responsible for it ? These questions are interesting not only from a theoretical point of view but also because of potential applications. Indeed, because of this hysteresis cycle, spin-conversion compounds appear as two-levels systems and the nanoparticles that present this hysteresis can be used as electronic components [18, 19].

M. Sorai and S. Seki ( 1974) [20] measured the heat capacities of  $[Fe(phen)_2(NCS)_2]$  and  $[Fe(phen)_2(NCSe)_2]$  crystals. These molecules are spin-conversion molecules. They concluded that "there is significant coupling between electronic state and phonon system" and that excitation of phonons is much easier in the high temperature phase. In order to take into account the results of Sorai and Seki, J. A. Nasser (2001) [21] assumed that the elastic force constant of the spring linking two molecules first neighbours in a crystal of spin conversion molecules depends on the electronic states of both molecules. The value of this elastic force constant is  $\lambda$  when both molecules are in the (LS) level and  $\nu$  when they are both in the (HS) one, with  $\nu < \lambda$ . With this last condition phonon system favours the (HS) level while  $\Delta$  favours the (LS) one.

Kate L. Ronayne et al. (2006) [22] determined by DFT calculations and from different experimental results the values of the intramolecular vibration frequencies of the molecule  $[Fe(phen)_2(NCS)_2]$  when this molecule is in the (LS) and (HS) levels. They found that these values are generally smaller when the molecule is in the (HS) level.

Previously, J. A. Nasser et al. (2007) [23] studied the case of a single molecule of  $[Fe(phen)_2(NCS)_2]$ , taking into account the results of Ronayne et al.. They showed that the molecule passes without hysteresis, from the (LS) level to the (HS) one when its temperature varies.

Now, we study the thermal behavior of two identical spin-conversion molecules linked by a chemical bond. We assume that i) the elastic force constant of the spring which exists between the two molecules depends on the electronic state of both molecules and that ii) there are in each molecule  $p$  independent linear harmonic oscillators.

For the following, each molecule is designated by atom and the set of two molecules is designated by molecule.

In Section 2, we present the theoretical study. In Section 3 we give the results obtained by the numerical study, and the last Section is devoted to discussion and conclusion. In the Appendix we establish approximate relationships that allow us to see where each parameter comes into play.

We recall that the study of the chemical bond between two atoms as part of the adiabatic approximation leads to the presence between both atoms of a spring-like and that the elastic force constant of this spring depends on the quantum states of the electrons involved in the bond [24].

The classical approximation cannot be used in the present study, because the model is based on the variation in the frequency of harmonic oscillators (see statistical physics cours and compare [21] and [25]).

## 2 Theoretical Study

### 2.1 Hamiltonian and Partition function

Consider a system of  $N$  identical molecules in contact with a heat reservoir at the absolute temperature  $T$ . We do not take into account the degrees of freedom of translation and of rotation of the molecules. And we consider the interaction between the molecules to be negligible.

Each molecule is made up of two identical atoms (1) and (2) linked by a chemical bond. Let us call  $k_{12}$  the elastic force constant of the spring that acts between both atoms. The atoms oscillate around their equilibrium position with the frequency  $\omega_{12}$  given by

$$\omega_{12} = \sqrt{\frac{2k_{12}}{m_a}} \quad (1)$$

where  $m_a$  is the mass of an atome and  $m_a/2$  is the reduced mass of the two atoms. The relation (1) can be established by means of classical mechanics [26].

The eigen values of the Haliltonian of vibrations  $\hat{H}_{vib12}$  are  $\hbar\omega_{12} (n_{12} + \frac{1}{2})$

with  $n_{12} = 0, 1, 2, \dots \infty$  and where  $\hbar$  is the Planck's constant divided by  $2\pi$ . The

partition function associated to the Hamiltonian  $\hat{H}_{vib12}$  is

$$z_{12vib} = \frac{1}{2 \sinh \left( \beta \frac{\hbar \omega_{12}}{2} \right)} \quad (2)$$

We recall that

$$\sum_{n=0,1,2,\dots} e^{-\beta \hbar \omega (n + \frac{1}{2})} = \frac{1}{2 \sinh \left( \beta \frac{\hbar \omega}{2} \right)} \quad (3)$$

with  $\beta = \frac{1}{k_B T}$  and where  $k_B$  is the Boltzmann constant.

We assume that each atom has two energy levels separated by  $\Delta$ . The fundamental level is not degenerated while the excited one has the degeneracy  $r$ . We associate the fictitious spin  $\hat{\sigma}_i$  to the atom ( $i$ ) ( $i = 1, 2$ ) and we assume that  $\hat{\sigma}_i$  has two eigenvalues  $\sigma_i = \pm 1$ . The degeneracy  $r$  comes from an other space of states.

The spin Hamiltonian of the atom ( $i$ ) can be written

$$\hat{H}_{sp}(i) = \frac{\Delta}{2} \hat{\sigma}_i \quad (4)$$

and the spin Hamiltonian of the molecule is

$$\hat{H}_{sp} = \frac{\Delta}{2} (\hat{\sigma}_1 + \hat{\sigma}_2) \quad (5)$$

The eigen values of the operator  $\hat{m} = \hat{\sigma}_1 + \hat{\sigma}_2$  are  $m = -2, 0, 2$ . The corresponding eigen kets are  $|-2\rangle = |-1, -1\rangle$ ,  $|0^{(1)}\rangle = |-1, 1\rangle$ ,  $|0^{(2)}\rangle = |1, -1\rangle$  and  $|2\rangle = |1, 1\rangle$ . In the brackets the first number is the value of  $\sigma_1$  and the second that of  $\sigma_2$ . The two kets  $|0^{(1)}\rangle$  and  $|0^{(2)}\rangle$  are the eigen states of the eigen value  $m = 0$ . The eigen values of the Hamiltonian  $\hat{H}_{sp}$  are  $-\Delta$ ,  $0$  and  $\Delta$  and the corresponding eigen kets are those of  $\hat{m} = \hat{\sigma}_1 + \hat{\sigma}_2$ .

The eigen values of the Hamiltonian  $\hat{H}_{sp} + \hat{H}_{vib12}$  are :

$$\begin{aligned} -\Delta + \hbar \omega_{12} \left( n_{12} + \frac{1}{2} \right), & \text{ with } n_{12} = 0, 1, 2, \dots \infty \\ \hbar \omega_{12} \left( n'_{12} + \frac{1}{2} \right), & \text{ with } n'_{12} = 0, 1, 2, \dots \infty \\ \Delta + \hbar \omega_{12} \left( n''_{12} + \frac{1}{2} \right), & \text{ with } n''_{12} = 0, 1, 2, \dots \infty \end{aligned} \quad (6)$$

Taking into account the degeneracy  $r$  and that of the eigen value  $m = 0$ , the partition function  $z_{spvib12}$  associated to the Hamiltonian  $\hat{H}_{sp} + \hat{H}_{vib12}$  is

$$z_{spvib12} = (e^{\beta \Delta} + 2r + r^2 e^{-\beta \Delta}) \frac{1}{2 \sinh \left( \beta \frac{\hbar \omega_{12}}{2} \right)} \quad (7)$$

As the Hamiltonians  $\hat{H}_{sp}$  and  $\hat{H}_{vib12}$  are independent, the partition function  $z_{spvib12}$  is the product of the partition functions associated with each of the two Hamiltonians.

Now we introduce the following assumptions :

i) We assume that the value of the elastic force constant  $k_{12}$  depends on the electronic states of the atoms. This elastic force constant is equal to  $\lambda$  when both atoms are in their fundamental level ( that corresponds to the state  $|-2\rangle$ ), to  $\nu$  when they are both in their excited level ( that corresponds to the state  $|2\rangle$ ) and to  $\mu$  when the two atoms are not in the same level ( that corresponds to the states  $|0^{(1)}\rangle$  and  $|0^{(2)}\rangle$ ). This assumption can be written as following (2001) [21] :

$$k_{12} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4}(\sigma_1 + \sigma_2) + \frac{\lambda - 2\mu + \nu}{4}\sigma_1\sigma_2 \quad (8)$$

We assume

$$\lambda \geq \nu \quad (9)$$

and

$$\mu = \frac{\lambda + \nu}{2} \quad (10)$$

The relation (8) introduces a coupling between the fictious spins and the vibrations of the molecule. Taking into account this coupling, the partition function becomes

$$(z_{spvib12})_{coupl} = e^{\beta\Delta} \frac{1}{2 \sinh(\beta \frac{\hbar\omega_{--}}{2})} + \frac{2r}{2 \sinh(\beta \frac{\hbar\omega_{+-}}{2})} + r^2 e^{-\beta\Delta} \frac{1}{2 \sinh(\beta \frac{\hbar\omega_{++}}{2})} \quad (11)$$

where

$$\omega_{--} = \sqrt{2 \frac{\lambda}{m}} \quad (12)$$

$$\omega_{+-} = \omega_{-+} = \sqrt{2 \frac{\mu}{m}} = \omega_{--} - \sqrt{\frac{\mu}{\lambda}} \quad (13)$$

and

$$\omega_{++} = \sqrt{2 \frac{\nu}{m}} = \omega_{--} - \sqrt{\frac{\nu}{\lambda}} \quad (14)$$

ii) We assume also that in each atom there are  $p$  identical and independent one-dimensional harmonic oscillators. The frequency value of one oscillator is  $\omega_{int}$  when the atom is in its fundamental level and  $\tilde{\omega}_{int}$  when it is in its excited

one. With this new assumption the partition function of the molecule becomes

$$z_{mol} = \frac{e^{\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{-}}{2})} \left( \frac{1}{2 \sinh(\beta \frac{\hbar\omega_{int}}{2})} \right)^{2p} + \frac{2r}{2 \sinh(\beta \frac{\hbar\omega_{-+}}{2})} \left( \frac{1}{2 \sinh(\beta \frac{\hbar\omega_{int}}{2})} \right)^p \left( \frac{1}{2 \sinh(\beta \frac{\hbar\tilde{\omega}_{int}}{2})} \right)^p + \frac{r^2 e^{-\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{++}}{2})} \left( \frac{1}{2 \sinh(\beta \frac{\hbar\tilde{\omega}_{int}}{2})} \right)^{2p} \quad (15)$$

Factorizing  $\left( \frac{1}{2 \sinh(\beta \frac{\hbar\omega_{int}}{2})} \right)^{2p}$  in the relation (15), we obtain

$$z_{mol} = \left( \frac{1}{2 \sinh(\beta \frac{\hbar\omega_{int}}{2})} \right)^{2p} z'_{mol} \quad (16)$$

with

$$z'_{mol} = \frac{e^{\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{-}}{2})} + \frac{2r R_{vib}}{2 \sinh(\beta \frac{\hbar\omega_{-+}}{2})} + \frac{r^2 R_{vib}^2 e^{-\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{++}}{2})} \quad (17)$$

and

$$R_{vib} = \left( \frac{2 \sinh(\beta \frac{\hbar\omega_{int}}{2})}{2 \sinh(\beta \frac{\hbar\tilde{\omega}_{int}}{2})} \right)^p \quad (18)$$

In the relation (16), the partition function  $z_{mol}$  appears as that of two independent systems : a system of  $2p$  identical and independent harmonic oscillators which vibrate with the frequency  $\omega_{int}$  and the system of the two fictitious spins  $\hat{\sigma}_1$  and  $\hat{\sigma}_2$  coupled to the vibrations of the molecule. We are concerned with  $z'_{mol}$ .

## 2.2 Probabilities and partial Gibbs-potentials

As the partition function  $z'_{mol}$  depends on the intensive parameters  $T$  and  $\Delta$ , the thermodynamic potential associated to  $z'_{mol}$  is the free enthalpy, or the Gibbs potential, denoted  $g$ . We have

$$g = -k_B T \ln(z'_{mol}) \quad (19)$$

Let  $\langle \hat{m} \rangle$  be the thermal mean value of the operator  $\hat{\sigma}_1 + \hat{\sigma}_2$ ,

$$\langle \hat{m} \rangle = \langle \hat{\sigma}_1 + \hat{\sigma}_2 \rangle \quad (20)$$

Accordind to the Hamiltonian  $\hat{H}_{sp}$ , relation (5),  $\langle m \rangle$  is the extensive parameter associatedn to  $\frac{\Delta}{2}$ . So we have

$$\langle \hat{m} \rangle = \frac{\partial g}{\partial \frac{\Delta}{2}} \quad (21)$$

and then

$$\langle \hat{m} \rangle = \frac{1}{z'_{mol}} \left( \frac{-2e^{\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{--}}{2})} + \frac{2r^2 R_{vib}^2 e^{-\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{++}}{2})} \right) \quad (22)$$

Let us introduce the parameters  $a_1$ ,  $a_2$  and  $a_3$  defined by

$$a_1 = \frac{e^{\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{--}}{2})} \quad (23)$$

$$a_2 = \frac{2r R_{vib}}{2 \sinh(\beta \frac{\hbar\omega_{-+}}{2})} \quad (24)$$

and

$$a_3 = \frac{r^2 R_{vib}^2 e^{-\beta\Delta}}{2 \sinh(\beta \frac{\hbar\omega_{++}}{2})} \quad (25)$$

The partition function  $z'_{mol}$  can be writen

$$z'_{mol} = a_1 + a_2 + a_3 \quad (26)$$

and the mean value  $\langle \hat{m} \rangle$  is given by

$$\langle \hat{m} \rangle = \frac{1}{z'_{mol}} (-2a_1 + 2a_3) \quad (27)$$

We introduce three thermodynamic states (or phases) : The thermodynamic state (2) that takes into account all the vibration energy levels associated with the eigen value  $m = 2$  and likewise the thermodynamic states (0) and (-2).

From relation (22) we see that the thermal probability to find the system in the quantum state  $|-2\rangle$ , that is in the thermodynamic state (-2) is

$$P(|-2\rangle) = P(-2) = \frac{a_1}{z'_{mol}} \quad (28)$$

Likewise

$$P(|2\rangle) = P(2) = \frac{a_3}{z'_{mol}} \quad (29)$$

and

$$P\left(\left|0^{(1)}\right\rangle \text{ and } \left|0^{(2)}\right\rangle\right) = P(0) = \frac{a_2}{z'_{mol}} \quad (30)$$



While  $z'_{mol}$  corresponds to the sum  $\sum_{(l)} e^{-\beta E_l}$  over all the microscopic states  $(l)$  of the molecule, the parameter  $a_1$  corresponds to the sum over all microscopic states for which the eigen value  $m$  is equal to  $-2$ , the sum is made over the energy levels of the oscillators. For this set of microscopic states one introduce the partial Gibbs potential  $g(-2)$

$$g(-2) = -k_B T \ln(a_1) \quad (31)$$

In the same way we define the partial Gibbs potential  $g(0)$  by

$$g(0) = -k_B T \ln(a_2) \quad (32)$$

and the partial Gibbs potential  $g(2)$  by

$$g(2) = -k_B T \ln(a_3) \quad (33)$$

From the relations (31- 33), we have

$$a_1 = \exp\left(-\frac{g(-2)}{k_B T}\right) \quad (34)$$

$$a_2 = \exp\left(-\frac{g(0)}{k_B T}\right) \quad (35)$$

and

$$a_3 = \exp\left(-\frac{g(2)}{k_B T}\right) \quad (36)$$

According to the relations (28-30) we see that between the three eigen values  $-2$ ,  $0$  and  $2$  the most probable is the one whose partial Gibbs potential is the smallest.

### 3 Numerical study

#### 3.1 Reduced parameters

We take  $\lambda$  as the unit of elastic force constant and  $\hbar\omega_{-}$  as the unit of energy. We then introduce the reduced energy gap

$$\delta = \frac{\Delta}{\hbar\omega_{-}} \quad (37)$$

the reduced temperature

$$t = \frac{k_B T}{\hbar\omega_{-}} \quad (38)$$

and the following reduced parameters

$$x = \frac{\nu}{\lambda} \quad (39)$$

$$zz = \frac{\omega_{int}}{\omega_{--}} \quad (40)$$

$$\tilde{x} = \frac{\tilde{\omega}_{int}}{\omega_{int}} \quad (41)$$

### 3.2 Results

The numerical study is done with  $r = 5$ ,  $zz = 1.2$ ,  $\tilde{x} = 0.9$ ,  $p = 2$ ,  $x = 0.1$ .

With  $\tilde{x}$  and  $x$  smaller than the unit the values of the vibration frequencies are lower when the atoms are in the excited level than when they are in the fundamental one what favours the excited level.

The values of the intramolecular vibration frequencies of a molecule depend on the masses of a few atoms in the molecule while the value of the intermolecular vibration frequency depend on the masses of all atoms in the molecules. For this reason, we chose  $\omega_{int}$  larger than  $\omega_{--}$ . So  $zz > 1$ .

The value of the parameter  $r$  is  $2S + 1$  with  $S = 2$ .

As  $R_{vib}$  is higher than the unit and as  $\omega_{++}$  is smaller than  $\omega_{--}$ , the vibrations favour  $a_3$ , that is the state (2), while the parameter  $\Delta$  favours  $a_1$ , that is the state (-2).

The reduced temperature value 0.001, corresponds to the 0K temperature.

#### 3.2.1 Case $\delta = 0.35$

The thermal variations of the partial Gibbs potentials  $g(-2)$ ,  $g(0)$  and  $g(2)$  for  $\delta = 0.35$  are shown in Figure 1. From this Figure we see that

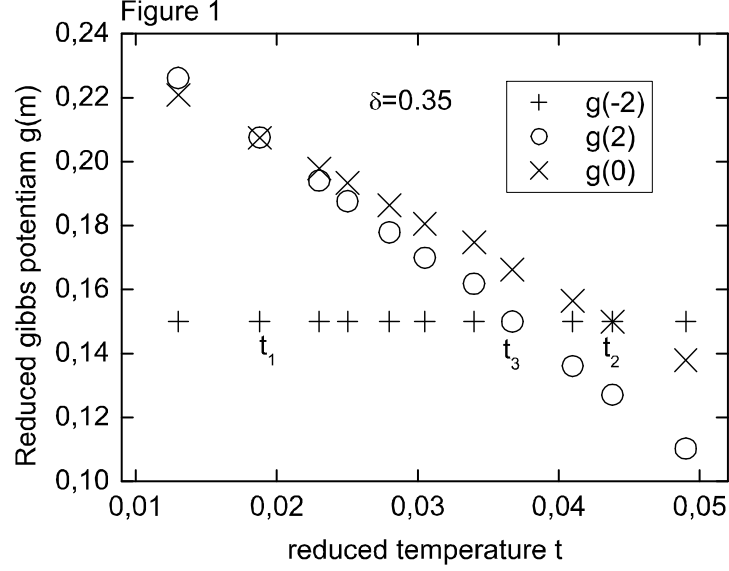
$$g(-2) < g(0) < g(2) \quad \text{for } 0.001 \leq t < t_1 \quad (42)$$

and that

$$g(-2) > g(0) > g(2) \quad \text{for } t > t_2 \quad (43)$$

So, the Gibbs potential  $g(m)$ , considered as a function of the eigen value  $m$ , is an increasing function of  $m$  below  $t_1$  and a decreasing function of  $m$  above  $t_2$ . On Figure 1 we see that  $g(0)$  is higher than  $g(2)$  above  $t_1 = 0.0188$  and smaller than  $g(-2)$  above  $t_2 = 0.0438$ .

There are two behaviors :



i) Below  $t_1$  and above  $t_2$ .

Below  $t_1$  and above  $t_2$  the molecules occupy the thermodynamic states  $(-2)$ ,  $(0)$  and  $(2)$  according to the probabilities  $P(-2)$ ,  $P(0)$  and  $P(2)$ , given in relations (28-30). The value of  $\langle \hat{m} \rangle$  is then calculated using relation (22). With relation (22),  $\langle \hat{m} \rangle$  is an increasing function of temperature below  $t_1$  and above  $t_2$ .

Figure 1. Thermal variations of the partial Gibbs potential  $g(m)$  for  $\delta = 0.35$  and  $m = -2, 0, 2$ . For the temperature values of the Figure,  $2 \sinh(\beta \frac{\hbar\omega_{--}}{2}) \simeq \exp(\beta \frac{\hbar\omega_{--}}{2})$  and  $g(-2) \simeq 0.5 - \delta$ .

ii) Between  $t_1$  and  $t_2$ .

**Stable, metastable and unstable state.** Between  $t_1$  and  $t_2$ ,  $g(0)$  appears as a maximum. Indeed

$$g(0) > g(-2) \text{ and } g(0) > g(2) \quad \text{for } t_1 < t < t_2 \quad (44)$$

For this reason the thermodynamic state  $(0)$  is unstable and the molecules do not occupy this state. Due to fluctuations, all the molecule are in the state  $(-2)$  when  $g(-2) < g(2)$ . Indeed, in this case, the energy barrier  $g(0) - g(-2)$  is

larger than the energy barrier  $g(0) - g(2)$ . So, if a fluctuation is large enough to exceed barrier  $g(0) - g(-2)$  and thus to allow molecules that are in state  $(-2)$  to pass into state  $(2)$ , a smaller fluctuation is required to exceed barrier  $g(0) - g(2)$  and thus to allow molecules that are in state  $(2)$  to pass into state  $(-2)$ . As the probability of fluctuations falls quickly with increasing amplitude of fluctuations, then we can expect that the molecules spend almost all the time in the state  $(-2)$  [27]. This state is thus called the stable state and the state  $(2)$  is called the metastable state. Likewise, when  $g(2) < g(-2)$  all the molecules are in the state  $(2)$  which is the stable state.

As shown in Figure 1, the partial Gibbs-potentials  $g(-2)$  and  $g(2)$  are equal at  $t_3 = 0.0367$  and the stable state is the state  $(-2)$  for  $t < t_3$  and the state  $(2)$  for  $t > t_3$ .

When all the molecules are in state  $(m)$ , with  $m = -2$  or  $2$ , the mean value  $\langle \hat{m} \rangle$  is equal to  $m$ .

**Delay in changing state** Suppose the system is in state  $(-2)$  at a temperature between  $t_1$  and  $t_3$ . Heating the system, it remains in this state and its temperature increases. At  $t_3$  the system can stay in the state  $(-2)$  instead of being shared between the state  $(-2)$  and the state  $(2)$  that are both stable. Then, heating the system, its temperature can increase to values higher than  $t_3$  and it finds itself in the state  $(-2)$  which is now metastable. Finally, the system passes into state  $(2)$  at a temperature  $t_3 + \Delta t$  between  $t_3$  and  $t_2$ .

Likewise, suppose the system is in state  $(2)$  at a temperature between  $t_3$  and  $t_2$ . Cooling the system, it passes into state  $(-2)$  at a temperature  $t_3 - \Delta t'$  between  $t_3$  and  $t_1$ .

**Role of  $k_B T$**  We assume that the amplitude of fluctuations is of the order of  $k_B T$ . Consequently we must compare the thermal energy  $k_B T$  to the quantities  $g(0) - g(-2)$  and  $g(0) - g(2)$ . If the barrier  $g(0) - g(-2)$  is higher than  $k_B T$ , the system cannot leave the state  $(-2)$  even if this state is metastable. Likewise, the system cannot leave the state  $(2)$  if the barrier  $g(0) - g(2)$  is higher than  $k_B T$ .

The thermal variations of the quantities  $g(0) - g(-2)$  and  $g(0) - g(2)$  and that of  $k_B T$  are shown in Figure 2. In this Figure, the barrier  $g(0) - g(2)$  is lower than  $k_B T$  for any temperature between  $t_1$  and  $t_2$ , while the barrier  $g(0) - g(-2)$  is lower than  $k_B T$  for  $t > t_4$ , with  $t_4 = 0.0305$ . It is interesting to note that  $t_4$  is less than  $t_3$ .

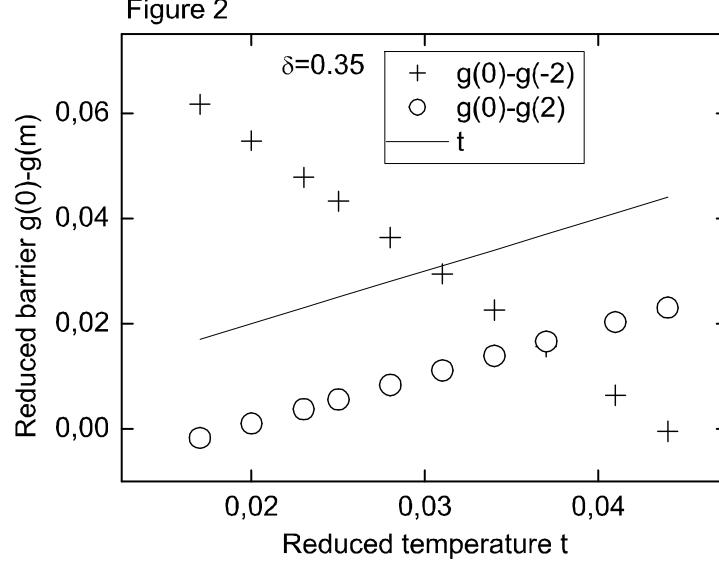
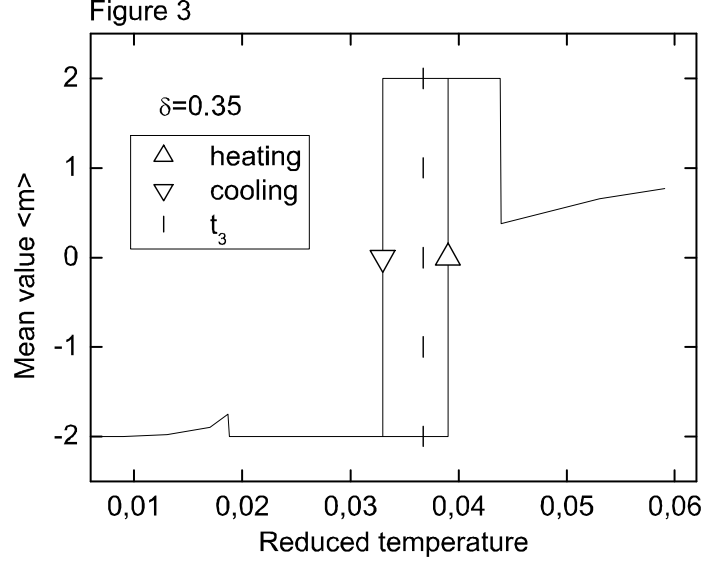


Figure 2. Thermal variations of the reduced values of the barriers  $g(0) - g(2)$  and  $g(0) - g(-2)$  for  $\delta = 0.35$  and  $t_1 \leq t \leq t_2$ . The reduced value of  $k_B T$  is  $t$ . The barrier  $g(0) - g(-2)$  is equal to  $k_B T$  at  $t_4 = 0.0305$ .

**Hysteresis cycle** The thermal behaviour of the parameter  $\langle \hat{m} \rangle$  in the diagram  $(\langle m \rangle, t)$  est shown in Figure 3.

Figure 3. Hysteresis cycle for  $\delta = 0.35$  in the  $(\langle m \rangle, t)$  diagram. The stable state is the state  $(-2)$  below  $t_3$  and the state  $(2)$  above  $t_3$ . The system change state at  $t_3 + \Delta t$  and at  $t_3 - \Delta t'$ . We recall that  $t_1 = 0.0188$ ,  $t_2 = 0.0438$  and  $t_3 = 0.0367$ .

Let us start from the initial temperature  $t = 0.059$ , greater than  $t_2$ . Using relation (22), we obtain  $\langle \hat{m} \rangle = 0.771$  for this temperature. Cooling the system, its temperature and  $\langle \hat{m} \rangle$  decreases. At  $t_2$ , the value of  $\langle \hat{m} \rangle$  calculated with relation (22) is 0.373. But, at  $t_2$ , the molecules go into the stable state  $(2)$ . Indeed, those in state  $(0)$  leave this state become unstable and those in state  $(-2)$  leave this state become metastable. The molecules can leave the state  $(-2)$



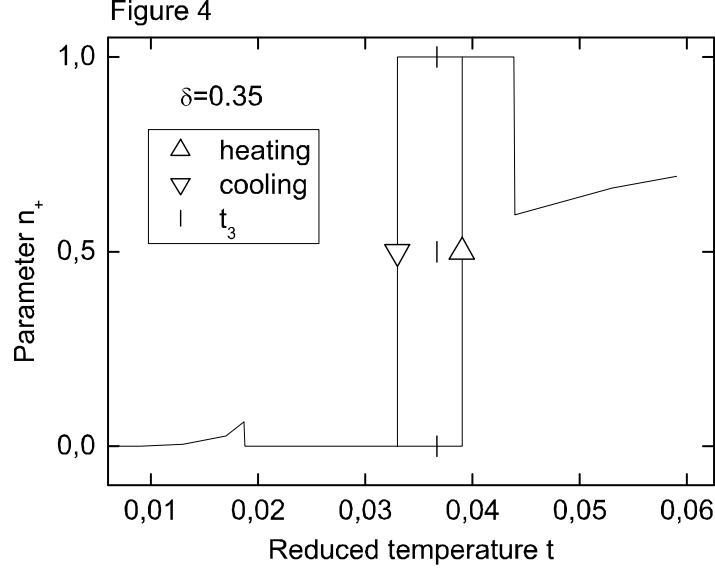
because the barrier  $g(0) - g(-2)$  is smaller than  $k_B T$ . So, at  $t_2$  the system is in the stable state (2) and  $\langle \hat{m} \rangle = 2$ . There is a discontinuity in  $\langle \hat{m} \rangle$  equal to 1.627.

Cooling the system, it remains in the state (2) and its temperature decreases down to  $t_3 - \Delta t'$ . At this temperature the system passes into the state (-2) which is the stable state. It can pass because the barrier  $g(0) - g(2)$  is smaller than  $k_B T$ . So, at  $t_3 - \Delta t'$  there is a discontinuity in  $\langle \hat{m} \rangle$  equal to -4.

Cooling the system it remains in the state (-2) and its temperature decreases down to  $t_1$ . Just below  $t_1$  the molecules occupy the states (-2), (0) and (2) with the probabilities  $P(-2)$ ,  $P(0)$  and  $P(2)$  and the value of  $\langle \hat{m} \rangle$ , calculated with the relation (22), is -1.743. So, at  $t_1$ , the discontinuity in  $\langle \hat{m} \rangle$  is then 0.257. Cooling the system below  $t_1$ , its temperature and the value of  $\langle \hat{m} \rangle$  decrease. At  $t = 0.001$ ,  $\langle \hat{m} \rangle = -2$ .

If now the system is heated, it will follow the same path as before, but it will go from state (-2) to state (2) at temperature  $t_3 + \Delta t$ . At this temperature it can change state because  $g(0) - g(-2)$  is smaller than  $k_B T$ .

In most experimental studies, it is the fraction of iron ion in the excited state ( $\sigma_i = 1$  for  $i$  equal 1 and 2) that is measured. In the present study, this parameter is the fraction of atoms in the excited level. This fraction  $n_+$  is given



by

$$n_+ = \frac{1}{2} \left( 1 + \frac{\langle \hat{m}_l \rangle}{2} \right) \quad (45)$$

Using relation (45) and Figure 3, we obtain the hysteresis cycle of the parameter  $n_+$ . This hysteresis cycle is shown in Figure 4.

Figure 4. Hysteresis cycle for  $\delta = 0.35$  in the  $(n_+, t)$  diagram. The parameter  $n_+$  is the fraction of atoms in the excited level.

### 3.2.2 Case $\delta = 0.30$

For  $\delta = 0.30$ ,  $g(0)$  is a maximum between the temperature values 0.001 and 0.02206. So,  $t_1 = 0.001$  and  $t_2 = 0.02206$ . But, in the case  $\delta = 0.30$ ,  $g(0)$  is not equal to  $g(2)$  at  $t_1$  as in case  $\delta = 0.35$ . The state  $(-2)$  is the stable state below  $t_3 = 0.00563$ . For  $t > t_2$ ,  $g(m)$  is a decreasing function of  $m$ .

As shown in Figure 5, the barrier  $g(0) - g(-2)$  is lower than  $k_B T$  for  $t$  greater than  $t_4 = 0.01538$ . As  $t_4$  is higher than  $t_3$ , the molecules can leave the state  $(-2)$  only above  $t_4$ . As shown in Figure 5, the barrier  $g(0) - g(2)$  is greater than  $k_B T$  for any temperature between 0.001 and  $t_2$ . It follows that the molecules cannot leave state  $(2)$  to go to state  $(-2)$ .

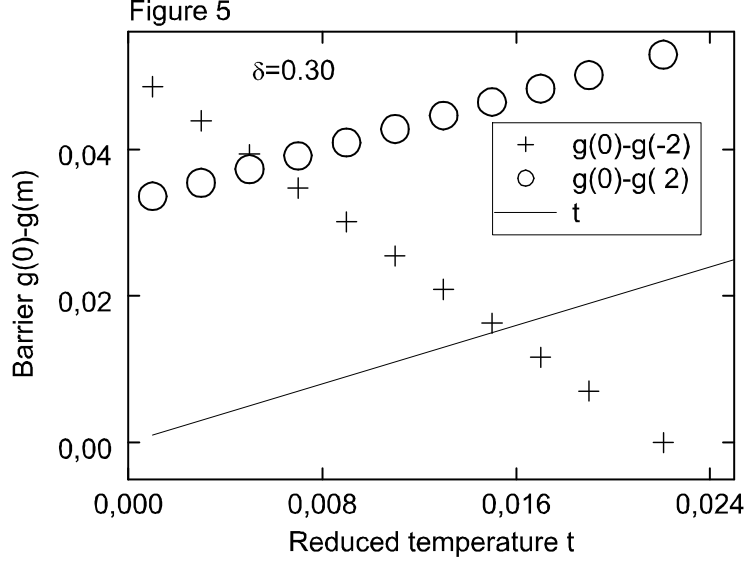


Figure 5. Thermal variations of the reduced values of the barriers  $g(0) - g(2)$  and  $g(0) - g(-2)$  and that of the thermal energy  $k_B T$  between  $t_1$  and  $t_2$ . For  $\delta = 0.30$ ,  $t_1 = 0.001$ . It worth to notice that  $t_4$  is larger than  $t_3$ .

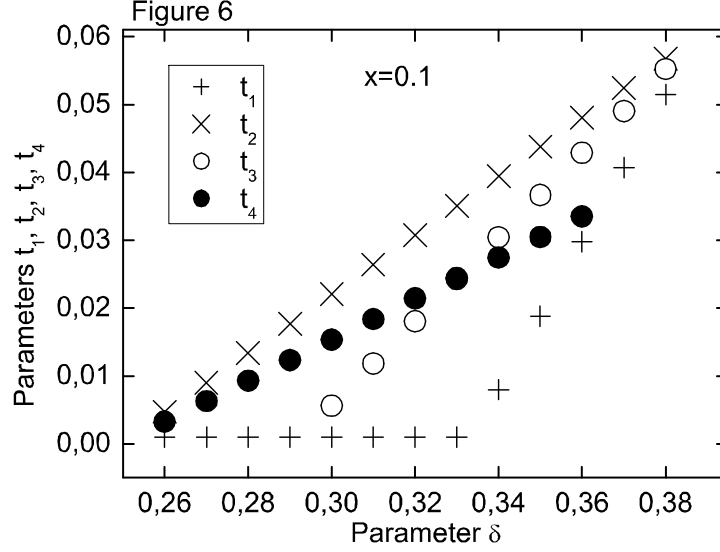
Let us start from the initial temperature  $t = 0.024$  greater than  $t_2$ . Using relation (22),  $\langle \hat{m} \rangle = 1.541$ . Cooling the system, its temperature and  $\langle \hat{m} \rangle$  decrease. Just above  $t_2$ , the value of  $\langle \hat{m} \rangle$  calculated with relation (22) is 1.538. As in the case  $\delta = 0.35$ , at  $t_2$  the system passes into the stable state (2) with a discontinuity in  $\langle \hat{m} \rangle$  equal to 0.462. Cooling the system, it remains in state (2) down to  $t_1$  while this state is metastable since  $t_3$ .

Now let us heat the system from the state  $t = 0.001$ ,  $\langle \hat{m} \rangle = 2$ . It remains in the state (2) up to  $t_2$ . Just above  $t_2$ , the molecules occupy the three states  $(-2)$ , (0) and (2) according to the probabilities  $P(-2)$ ,  $P(0)$  and  $P(2)$ , respectively.

Now suppose that the system is prepared in the state  $t = 0.001$ ,  $\langle \hat{m} \rangle = -2$ . Heating the system it remains in the state  $(-2)$  up to  $t_4 + \Delta t$ . At this temperature it passes in the state (2) and can no longer return to state  $(-2)$ .

It is clear that there is no hysteresis cycle for  $\delta = 0.30$ .





### 3.2.3 Varying $\delta$

The values of the parameters  $t_1$ ,  $t_2$ ,  $t_3$  and  $t_4$  for different values of  $\delta$  are shown in Figure 6.

For  $\delta = 0.38$ , there is an hysteresis cycle, but not for  $\delta = 0.39$ . So, the hysteresis cycle disappears when  $\delta$  is greater than a value  $\delta_{\max}$  between 0.38 and 0.39.

For  $\delta = 0.34$ , there is an hysteresis cycle and this case is the same as the case  $\delta = 0.35$ . For  $\delta = 0.33$ , there is no hysteresis cycle and this case is the same as the case  $\delta = 0.30$ . So, the system displays hysteresis cycle when  $\delta$  is greater than a value  $\delta_{\min}$  between 0.33 and 0.34, and smaller than  $\delta_{\max}$ .

As shown in Figure 6, the difference  $t_2 - t_1$  decreases when the parameter  $\delta$  tends toward  $\delta_{\max}$ , the same is true for the width of the hysteresis cycle. It worth noting that  $t_4$  is smaller than  $t_3$  for  $\delta \geq 0.34$ .

Figure 6. Variations with  $\delta$  of the values of the parameters  $t_1$ ,  $t_2$ ,  $t_3$  and  $t_4$ . For a given value to  $\delta$ ,  $g(0)$  is a maximum of the function  $g(m)$  for any temperature between  $t_1$  and  $t_2$  but it is not enough to have an hysteresis cycle.

## 4 Conclusion

The molecules can display an hysteresis cycle for some values of  $\delta$ . These values depend on those of the model parameters. For example, with  $x = 0.1$  and  $\tilde{x} = 0.9$  we found that the function  $g(m)$  had no maximum for  $\delta = 0.39$ . But, with  $x = 0.1$  and  $\tilde{x} = 0.86$  there is an hysteresis cycle.

If the elastic force constant  $k_{12}$  does not depend on the electronic states of the two atoms, i.e.  $x = 1$ , the function  $g(m)$  does not have a maximum. The range of values of  $\delta$  leading to an hysteresis cycle can be expected to decrease when  $x$  increases [21].

Studying the nanoparticles of the complex  $Fe(pyrazine)\{Pt(CN)_4\}$ , Florence Voltaron et al. [16] have found that the amount of  $Fe^{+2}$  ions remaining in the excited level at low temperature is larger for the smaller particles. This experimental result can correspond to the cases where the molecules remain in the state (2) ( see case  $\delta = 0.30$ ).

It is recalled that the excited level of an atom is degenerated. Also, when at  $0K$  there are atoms in the excited level, the entropy of the system is not zero which is not in agreement with the third law of thermodynamics. However, as the degeneracy is due to the  $3d$  electrons spins, any magnetic field, for example the earth magnetic field, can suppress the degeneracy and restore the respect of this law.

Concerning spin conversion molecules, the results obtained in this study support the statements of J.-F. Létard (2004) [19] that the molecular scale must be considered as the limit of the miniaturization of components used in working devices.

Finally, we would like to emphasize that, in magnetism, the coupling between spins is due to orbitals overlaps while, here, the coupling between the electronic quantum states of two molecules is due to vibrations.

We would like to thank H. T. Diep for our fruitful discussions and L. Chasagne for his support as director of LISV.

## 5 Author contribution statement

The author has done alone this study and has written alone this manuscript.

## 6 Appendix

### 6.1 Approximative relations

Approximative relations can allow to discuss the numerical results.

If we replace  $2 \sinh(x)$  by  $e^x$ , the relations (23), (24) and (25) become

$$a_1 \simeq e^{\beta \Delta} e^{-\beta \frac{\hbar \omega_{--}}{2}} \quad (1)$$

$$a_2 \simeq 2r R_{vib} e^{-\beta \frac{\hbar \omega_{+-}}{2}} \quad (2)$$

$$a_3 \simeq r^2 R_{vib}^2 e^{-\beta \Delta} e^{-\beta \frac{\hbar \omega_{++}}{2}} \quad (3)$$

For the parameter  $R_{vib}$  we have

$$R_{vib} \simeq \left( e^{\beta \frac{\hbar \omega_{int}}{2}} e^{-\beta \frac{\hbar \tilde{\omega}_{int}}{2}} \right)^p$$

So

$$\ln(R_{vib}) \simeq p \beta \frac{\hbar \omega_{int}}{2} \left( 1 - \frac{\tilde{\omega}_{int}}{\omega_{int}} \right) \quad (4)$$

Using reduced parameters, we obtain

$$-kT \ln(R_{vib}) \simeq -\frac{1}{2} p \, z z (1 - \tilde{x}) \quad (5)$$

and

$$g(-2) \simeq -\delta + \frac{1}{2} \quad (6)$$

$$g(0) \simeq -t \ln(2r) + b \quad (7)$$

$$g(2) \simeq -t \ln(r^2) + c + \delta \quad (8)$$

with

$$b = \frac{1}{2} \sqrt{\frac{1+x}{2}} - \frac{1}{2} p \, z z (1 - \tilde{x}) \quad (9)$$

$$c = \frac{1}{2} \sqrt{x} - p \, z z (1 - \tilde{x}) \quad (10)$$

The quantities  $g(0) - g(-2)$  and  $g(0) - g(2)$  are given by

$$g(0) - g(2) \simeq (\ln(r^2) - \ln(2r)) t + b - c - \delta \quad (11)$$

$$g(0) - g(-2) \simeq -\ln(2r) \, t + b - \frac{1}{2} + \delta \quad (12)$$

with

$$b - c = \frac{1}{2} \left( \sqrt{\frac{1+x}{2}} - \sqrt{x} + p \, z z (1 - \tilde{x}) \right) \quad (13)$$

$$b - \frac{1}{2} = \frac{1}{2} \left( \sqrt{\frac{1+x}{2}} - p \, z z (1 - \tilde{x}) - 1 \right) \quad (14)$$

It is easy to verify that for  $x$  comprised between 0 and 1,  $b - c$  is positive and  $b - \frac{1}{2}$  is negative. Moreover for  $r = 5$ ,  $\ln(r^2) - \ln(2r)$  is positive.

## 6.2 Sign of $g(0) - g(m)$ , for $m = \pm 2$ .

i) As can be seen in relation (11), the quantity  $g(0) - g(2)$  is an increasing function of the temperature  $t$ . When  $\delta$  is greater than  $b - c$ , this function is negative at  $t = 0$  and increases when the temperature increases. It becomes positive for  $t$  greater than  $t_1$  which is given by

$$t_1 = \frac{\delta - (b - c)}{\ln r^2 - \ln(2r)} \quad \text{with } \delta > b - c \quad (15)$$

When  $\delta$  is smaller than  $b - c$ , this function is positive at  $t = 0$  and it remains positive at any temperature.

So

$$\begin{aligned} g(0) - g(2) &> 0 \quad \text{for } t > t_1 \quad \text{when } \delta > b - c \\ \text{and for } t &\geq 0 \quad \text{when } \delta < b - c \end{aligned} \quad (16)$$

One can say that for  $\delta < b - c$ ,  $t_1$  is equal to zero.

ii) As can be seen in relation (12), the quantity  $g(0) - g(-2)$  is a decreasing function of the temperature  $t$ . If  $\delta$  is higher than  $\frac{1}{2} - b$ , this function is positive at  $t = 0$  and decreases when the temperature increases. This function becomes negative above  $t_2$  given by

$$t_2 = \frac{\delta - (\frac{1}{2} - b)}{\ln(2r)} \quad \text{with } \delta > \frac{1}{2} - b \quad (17)$$

When  $\delta$  is lower than  $\frac{1}{2} - b$ , the quantity  $g(0) - g(-2)$  is negative at  $t = 0$  and remains negative at any temperature. So,

$$g(0) - g(-2) > 0 \quad \text{for } t < t_2 \quad \text{when } \delta > \frac{1}{2} - b \quad (18)$$

One can show that

$$b - c > \frac{1}{2} - b \quad (19)$$

and from this relation we can show that

$$t_1 < t_2 \quad (20)$$

When  $g(0) - g(2)$  et  $g(0) - g(-2)$  are both positive,  $g(0)$  appears as a maximum between two minima and the state (0) is unstable state.

The parameters  $t_1$  and  $t_2$  are increasing linear functions of  $\delta$ . As  $(\ln(r^2) - \ln(2r))$  is smaller than  $\ln(2r)$ , the  $t_1$  function grows faster than the  $t_2$  function. Also there exists a value of  $\delta$  where these two functions are equal. This value called  $\delta_{\max}$  is given by

$$\delta_{\max} = \frac{1}{2\ln(2)} \left[ \ln(r) \left( b - c - \left( \frac{1}{2} - b \right) \right) + \ln(2) \left( b - c + \left( \frac{1}{2} - b \right) \right) \right] \quad (21)$$

When  $\delta$  is greater than  $\delta_{\max}$ ,  $g(0)$  is no longer a maximum.

## 7 Data Availability Statement :

No Data associated in the manuscript

## 8 References

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