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Molecules with two electronic energy levels :
thermal hysteresis
in a set of two molecules linked by a chemical
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 Δ 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 λ when both molecules are in the (LS) level and ν when they are both in the (HS) one, with $\nu < \lambda$. With this last condition phonon system favours the (HS) level while Δ 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 ω_{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 2π . 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

$$\sum_{n=0.1.2\dots} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = \frac{1}{2 \sinh\left(\beta \frac{\hbar\omega}{2}\right)} \quad (3)$$

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 Δ . 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 ($i = 1, 2$) 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 σ_1 and the second that of σ_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 Δ 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 λ when both atoms are in their fundamental level (that corresponds to the state $|-2\rangle$), to ν when they are both in their excited level (that corresponds to the state $|2\rangle$) and to μ 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 ω_{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 ω_{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 Δ , 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 $\hat{\sigma}_1 + \hat{\sigma}_2$,

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

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

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

and then

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

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 written

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

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

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

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 λ 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 Values of the parameters

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 ω_{int} larger than ω_{--} . So $zz > 1$.

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

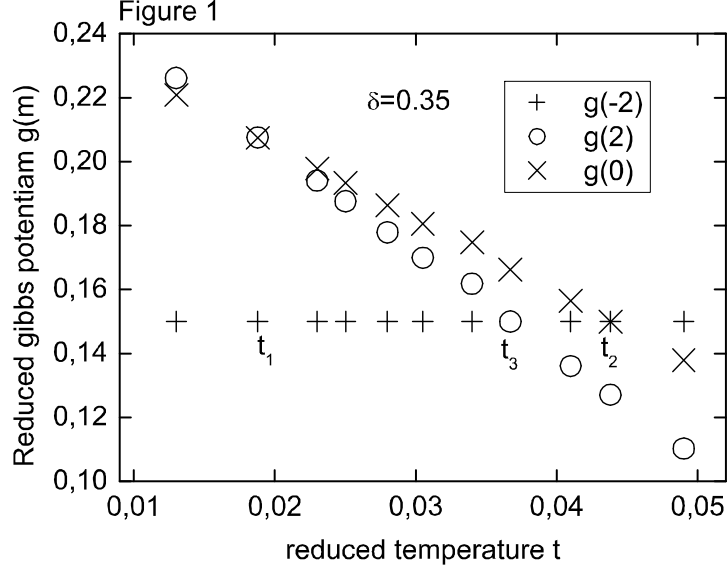
As R_{vib} is higher than the unit and as ω_{++} is smaller than ω_{--} , the vibrations favour a_3 , that is the state (2), while the parameter Δ favours a_1 , that is the state (-2).

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

4 Study of the 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.

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, $2 \sinh(\beta \frac{\hbar\omega_{--}}{2}) \simeq \exp\left(\beta \frac{\hbar\omega_{--}}{2}\right)$ and $g(-2) \simeq 0.5 - \delta$.



In this Figure we see that for t lower than $t_1 = 0.0188$, the Gibbs potential $g(m)$, considered as a function of the eigen value m , is an increasing function of m , that is

$$g(-2) < g(0) < g(2) \quad (42)$$

For t higher than $t_2 = 0.0438$, $g(m)$ is a decreasing function of m , that is

$$g(-2) > g(0) > g(2) \quad (43)$$

Between t_1 and t_2 , $g(0)$ appears as a maximum of the function $g(m)$.

There are two behaviors : t outside the interval (t_1, t_2) and $t_1 \leq t \leq t_2$.

4.1 $t < t_1$ or $t > t_2$

Below t_1 and above t_2 the molecules occupy the thermodynamique 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 .

4.2 $t_1 \leq t \leq t_2$

Between t_1 and t_2 , $g(0)$ appears as a maximum. Indeed

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

4.2.1 Stable, metastable and unstable state.

Callen's argument [27] It is known that studying a system some weak interactions are not included in the studied Hamiltonian [28, 29]. For example, nanoparticles of spin conversion molecules are obtained and studied experimentally in a liquid. Due to Brownian motion, the molecules of the liquid can collide with the nanoparticles. Generally, these interactions are not taken into account in the studied Hamiltonian but such small interactions are capable of inducing transitions between the states of the studied Hamiltonian. For systems in contact with a reservoir at constant temperature these transitions take place between the states of the global system, i.e. the studied system + the reservoir. Those small interactions tends to produce the thermal equilibrium but they also can randomly modify the value of the energy of the studied system and the values of other internal parameters. So these values fluctuate around equilibrium values.

According to H. B. Callen, in the case where the Gibbs potential of the studied system displays a maximum surrounded by two minima, the system "spends almost of this time in the more stable minimum (the deepest minimum)". In this case the variable on which depends the Gibbs potential is an extensive parameter. In the present study, we repeat Callen's argument and we justify it by solving the master equation.

As $g(0)$ is a maximum, 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). 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 $\langle \widehat{m} \rangle$ is equal to m .

Justification of Callen's argument Let us denote $(1), (2), (3)$ the states $(-2), (0), (2)$, respectively and $P_i(\tau)$, $i = 1, 2, 3$, the probability that the studied molecule is found in state (i) at time τ . With $j = 1, 2, 3$, the master equation is

$$\frac{dP_i}{d\tau} = \sum_{j \neq i} (P_j W_{ji} - P_i W_{ij}) \quad (45)$$

where the parameter W_{ji} is the transition probability per unit time from the state (j) to the state (i) . This parameter is matrix element between states of the global system (the thermostat + the studied molecule). It depends on the temperature T (or the reduced temperature t).

Using the relation

$$P_j W_{ji} = P_i W_{ij} \quad (46)$$

We deduce

$$\frac{W_{ij}}{W_{ji}} = \frac{P_j}{P_i} \quad (47)$$

As we study variations around the equilibrium we take for the right side of the equation (47) the values of relations (28), (29) and (30). So,

$$\frac{W_{ij}}{W_{ji}} = \frac{a_j}{a_i} \quad (48)$$

So,

$$\frac{W_{12}}{W_{21}} = \frac{a_2}{a_1} = \exp\left(-\frac{g(0) - g(-2)}{k_B T}\right) \quad (49)$$

$$\frac{W_{13}}{W_{31}} = \frac{a_3}{a_1} = \exp\left(-\frac{g(2) - g(-2)}{k_B T}\right) \quad (50)$$

$$\frac{W_{32}}{W_{23}} = \frac{a_2}{a_3} = \exp\left(-\frac{g(0) - g(2)}{k_B T}\right) \quad (51)$$

As $g(0) - g(-2)$ is positive, $W_{12} < W_{21}$. We take $W_{12} = 0$. Likewise, we take $W_{32} = 0$.

For $t_1 \leq t < t_3$, $g(2) - g(-2)$ is positive. We take $W_{13} = 0$. So the master equation becomes

$$\frac{dP_1}{d\tau} = W_{21}P_2 + W_{31}P_3 \quad (52)$$

$$\frac{dP_2}{d\tau} = -W_{21}P_2 - W_{23}P_2 \quad (53)$$

$$\frac{dP_3}{d\tau} = -W_{31}P_3 + W_{23}P_2 \quad (54)$$

The solution of the equation (53) is

$$P_2 = (P_2)_0 \exp(-(W_{21} + W_{23})\tau) \quad (55)$$

where $(P_2)_0$ is the initial value of P_2 . After some time of the order of τ_2 given by

$$\tau_2 = \frac{1}{W_{21} + W_{23}} \quad (56)$$

P_2 is equal to zero.

When $P_2 = 0$, the equation (54) becomes

$$\frac{dP_3}{d\tau} = -W_{31}P_3 \quad (57)$$

The solution of equation (57) is

$$P_3 = (P_3)_0 \exp(-W_{31}\tau) \quad (58)$$

where $(P_3)_0$ is the initial value of P_3 . After some time of the order of τ_3 given by

$$\tau_3 = \frac{1}{W_{31}} \quad (59)$$

P_3 is equal to zero. Then the equation (52) becomes

$$\frac{dP_1}{d\tau} = 0 \quad (60)$$

The solution of this equation is $P_1 = 1$.

For $t_3 < t \leq t_2$, as $g(-2)$ is lower than $g(2)$, it is W_{31} which is equal to zero and not W_{13} . We obtain $P_3 = 1$.

This calculation leads to the same result as Callen's argument.

4.2.2 Delay in changing state

From the precedent discussion, the studied molecule must change state at t_3 when the two Gibbs potentials $g(-2)$ and $g(2)$ are equal. It is the same situation as in the case of the phase change of a pure substance. However, it is known that the temperature of a liquid can be lowered below its freezing point without it becomes solid. In this case the pure substance remains in the liquid phase which is no longer the stable state. Likewise a liquid can exist above its boiling point. These phenomena, which have different causes, makes it possible to explain the

thermal hysteresis observed in certain first order phase transitions. We assume that this phenomenon plays role in the present study.

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 .

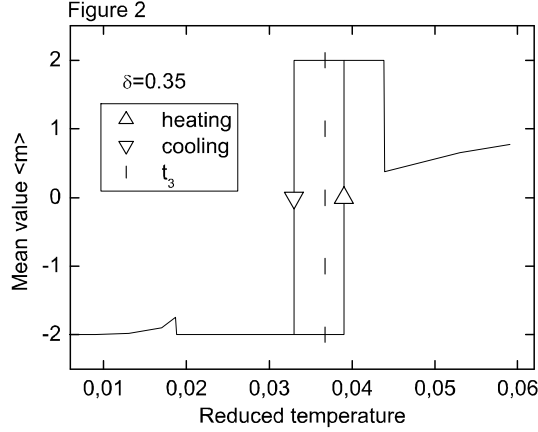
4.2.3 Hysteresis cycle

The thermal behaviour of the parameter $\langle \hat{m} \rangle$ in the diagram $(\langle m \rangle, t)$ is shown in Figure 2.

Figure 2. 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 which are in state (0) leave this state because it is unstable and those which are in state (-2) leave this state because it is metastable. 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. 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 $t = 0.001$, $\langle \hat{m} \rangle = -2$.

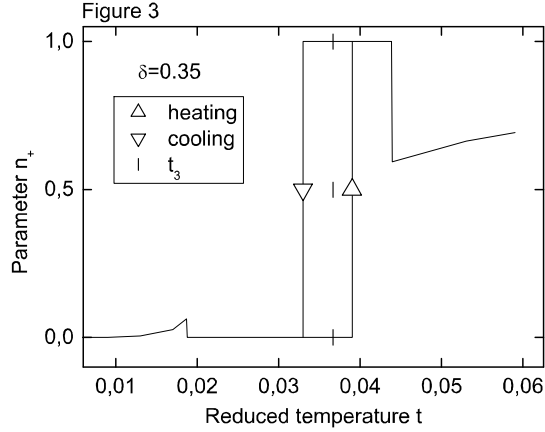
If now the system is heated, it will follow the same path as before, but it will go from state (-2) to state (2) at temperature $t_3 + \Delta t$.

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

$$n_+ = \frac{1}{2} \left(1 + \frac{\langle \hat{m} \rangle}{2} \right) \quad (61)$$

Using relation (61) and Figure 2, we obtain the hysteresis cycle of the parameter n_+ . This hysteresis cycle is shown in Figure 3.

Figure 3. Hysteresis cycle for $\delta = 0.35$ in the (n_+, t) diagram. The parameter n_+ is the fraction of atoms in the excited level.

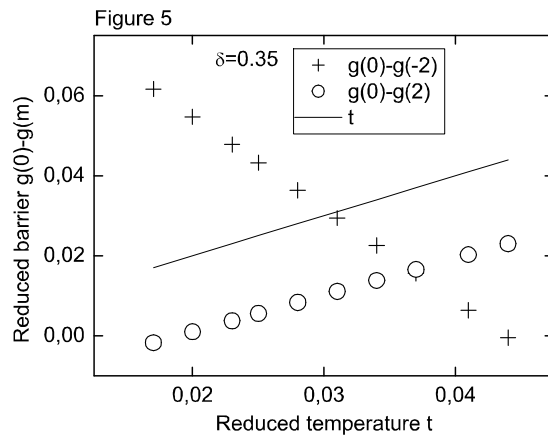
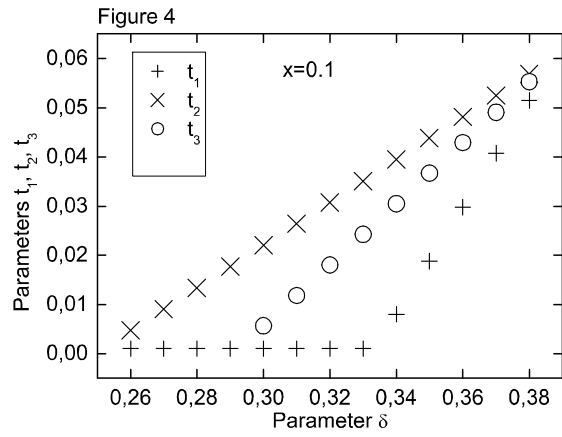


5 Discussion and Conclusion

We have shown that the molecules can display an hysteresis cycle for $\delta = 0.35$. The previous study can be done for other values of δ for which $g(0)$ is a maximum. These values are shown in Figure 4. In this Figure we see that for certain values of δ the temperature t_1 is equal to zero.

Figure 4. Variations with δ of the values of the parameters t_1 , t_2 and t_3 . For a given value of δ , $g(0)$ is a maximum of the function $g(m)$ for any temperature between t_1 and t_2 .

To solve the master equation of evolution we took W_{12} and W_{32} equal to zero. This approximation is all the better as the quantities $\frac{g(0)-g(\pm 2)}{k_B T}$ are large. The thermal variations of the quantities $g(0) - g(2)$, $g(0) - g(-2)$ and $k_B T$ for δ equal to 0.35 and 0.30 are shown in the Figures 5 and 6, respectively. In these Figures we see that the approximation is better in case $\delta = 0.30$ than in case $\delta = 0.35$.



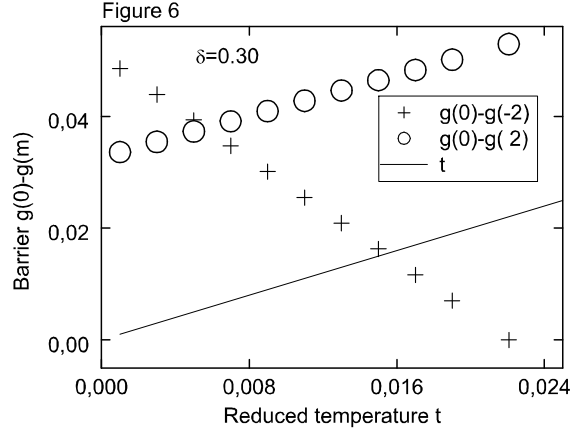


Figure 5. Thermal variations of the barriers $g(0) - g(2)$ and $g(0) - g(-2)$ for $\delta = 0.35$ and $t_1 \leq t \leq t_2$. The reduced value of $k_B T$ is t .

Figure 6. Thermal variations of the reduced values of the barriers $g(0) - g(2)$ and $g(0) - g(-2)$ for $\delta = 0.30$ and $t_1 \leq t \leq t_2$. The reduced value of $k_B T$ is t . In case $\delta = 0.30$, $t_1 = 0.001$ as shown in Figure 4.

It would be interesting to study the role of the other parameters of the model. We have verified that the function $g(m)$ does not have a maximum for $x = 1$, that is if the elastic force constant k_{12} does not depend on the electronic states of the two atoms. The range of values of δ leading to an hysteresis cycle can be expected to decrease when x increases [21].

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 orbital overlaps while the coupling between the electronic quantum states of two spin conversion 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.

6 Author contribution statement

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

7 Appendix

7.1 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

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

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

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

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

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

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

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

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.

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

So

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

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 δ 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 δ 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 δ . 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 δ where these two functions are equal. This value called δ_{\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 δ is greater than δ_{\max} , $g(0)$ is no longer a maximum.

8 Data Availability Statement :

No Data associated in the manuscript

9 References

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