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Hélène Bolvin [a] & Olivier Kahn [a]

[a] Laboratoire de Chimie Inorganique, URA 420, Université de Paris-Sud, 91405, Orsay, France

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COOPERATIVITY AND ANTICOOPERATIVITY IN SPIN TRANSITION COMPOUNDS; MACROSCOPIC APPROACH AND ORBITAL MODELIZATION.

Hélène BOLVIN and Olivier KAHN
Laboratoire de Chimie Inorganique, URA 420, Université de Paris-Sud, 91405 Orsay, France.

Abstract The intermolecular interaction parameter occuring in the thermodynamical approach of spin transition proposed by Slichter and Drickamer is analyzed at the microscopic level. Then, an orbital model is proposed, to estimate this microscopic interaction between two neighbouring spin transition molecules. It shows that there is a competition between the direct interaction between the two metal centers and the indirect interaction through the ligands.

INTRODUCTION

The phenomenon of thermally or pressure induced high-spin (HS) ↔ low-spin (LS) crossover in some transition metal compounds is now well documented [1,2,3,4]. Through various experimental techniques, notably susceptibility measurements and Mössbauer spectra, it has been shown that the transitions in the solid state can be either discontinuous or continuous.

Theoretical studies agree on the cooperative nature of the discontinuous transitions. However, they are all based on a phenomenological approach in which the microscopic nature of the intermolecular interactions is not analyzed. In this paper, we will point out that one of the factors of the cooperativity is the intermolecular electron-electron repulsion. First, the intermolecular interaction parameter occuring in the model of spin-transition proposed by Slichter and Drickamer[5] is interpreted at a microscopic level. Subsequently, a model is presented, based on molecular orbital calculations, showing that there is a competition between the direct interaction between the two metal centers and the indirect interaction through the ligands.

Up to now, we did not take into account the vibrations; but we think that the dynamical point of view can be further included in the model.

MACROSCOPIC APPROACH OF THE COOPERATIVITY

In the thermodynamical approach proposed by Slichter and Drickamer in 1972 , the Gibbs free energy G per mole of a spin transition system is written as:

$$G = (1 - x)\, G_L + x\, G_H + \Gamma\, x\, (1 - x) + R\, T\, (x \ln x + (1 - x) \ln (1 - x)) \qquad (1)$$

x is the molar fraction of high-spin compound, G_L and G_H are the molar Gibbs free energies of the LS and HS pure phases, respectively. The last term is the mixing entropy, and $\Gamma\, x\, (1 - x)$ stands for the excess Gibbs energy assuming a random distribution of the two species. Γ characterizes the cooperativity of the transition; with increasing positive values of Γ, the transition becomes more abrupt up to the appearance of a hysteresis. For negative values of Γ, the expression leads to soft transitions, for which the term "anticooperativity" has recently been coined [6].

This model has been further improved, by including the effect of phonons [7,8] and of crystal compressibility [9]. The phenomenon has also been described on the basis of domains[10,11].

Expression (1) can be obtained from a microscopic theory, by applying statistical mechanics; it can be shown that the excess energy of eq.(1) corresponds to an Ising type Hamiltonian, in the molecular field approximation. Γ is then related to the interaction parameter γ of the Ising Hamiltonian through:

$$\Gamma = N\, z\, \gamma \qquad (2)$$

z being the number of nearest neighbours and N the Avogadro constant. Thus, the macroscopic parameter Γ is directly related to interactions between two adjacent molecules.

ORBITAL MODELIZATION

We single out two molecules in the crystal, and we denote their total energies by E_{LL}, E_{HH} and E_{LH} according to whether they are both in the LS state, both in the HS state, and one in the HS, the other one in the LS, respectively. Then, γ can be expressed in the following way:

$$\gamma = E_{HL} - (E_{LL} + E_{HH})/2 \qquad (3)$$

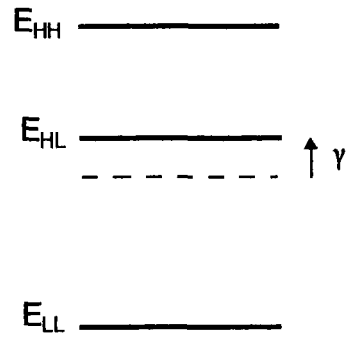

FIGURE 1 Relation between γ and the energies E_{LL}, E_{LH} and E_{HH}.

In a number of compounds showing an abrupt spin transition, e.g. $Fe(phen)_2(NCS)_2$ and $Fe(bipy)_2(NCS)_2$ (phen = 1,10-phenantroline and bipy = 2,2'-bipyridine), the π rings of two neighbouring molecules are parallel, at a distance of 3.8 Å[12]. These relative positions favour an interaction between the molecular orbitals of the ligands.

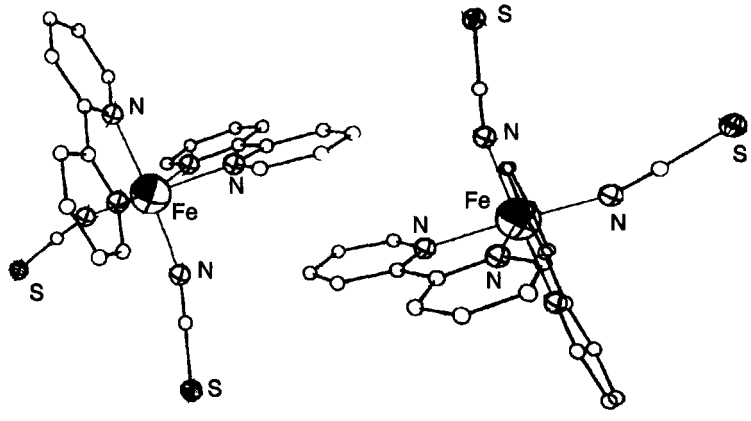

FIGURE 2 Relative positions of two nearest neighbour molecules in the lattice of $Fe(bipy)_2(NCS)_2$.

In a first time, we describe each molecule A and B by a four-orbital, four-electron system. For A, the molecular orbitals are, in increasing energy order,

π_A, a_1, a_2 and π_A^*. π_A and π_A^* represent orbitals whose main contributions are a bonding and an antibonding ligand orbital, respectively; a_1 and a_2 are two mainly metal orbitals. The former stands for the t_{2g} subset, the latter for the e_g subset. We suppose that the symmetries of the orbitals a_1 and a_2 are different, and that π_A and π_A^* have the same symmetry as either a_1 or a_2. The four orbitals are supposed to be eigenvectors of the Fock operator of the closed shell. In a first step, we describe the LS and HS states of one molecule using configuration interaction in the perturbation theory approach.

In this framework, the ground state reads:

$$|S_A^0\rangle = |\pi_A \bar{\pi}_A a_1 \bar{a}_1| \tag{4}$$

where $|\ |$ denotes a Slater determinant; x and $\bar{x}$ represent the spinorbitals of α and β spin, respectively. The first excited state is here a triplet, whose $m_s = 1$ component reads:

$$|T_A^0\rangle = |\pi_A \bar{\pi}_A a_1 a_2| \tag{4'}$$

The largest contribution to the configuration interaction is due to the following excited state (component $m_s = 1$):

$$|T_A^*\rangle = \left(|\pi_A \bar{\pi}_A^* a_1 a_2| - |\bar{\pi}_A \pi_A^* a_1 a_2|\right) / \sqrt{2} \tag{5}$$

This is one of the triplet states resulting from $|T_A^0\rangle$ with a $\pi_A \rightarrow \pi_A^*$ excitation.

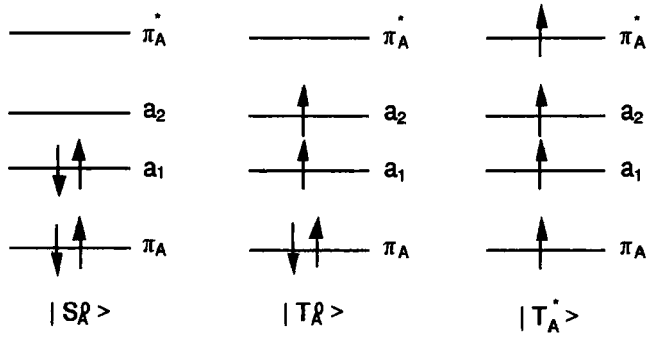

FIGURE 3 States of the four-orbital, four-electron system

Then, in first-order, the LS and HS state are described by the following wavefunctions

$$| S_A > = | S_A^0 > \quad \text{and} \tag{6}$$

$$| T_A > = | T_A^0 > - \frac{\left(j_{\pi 1}^0 - j_{\pi 2}^0 \right)}{F_{\pi^*} - F_\pi} | T_A^* > \qquad \text{with} \tag{6'}$$

$$j_{\pi k}^0 = \left\langle \pi_A(1)\, a_k(2) \left| \frac{1}{r_{12}} \right| \pi_A^*(1)\, a_k(2) \right\rangle \qquad k = 1, 2 \tag{7}$$

F_x being the eigenvalues of the Fock operator for the x orbital. It must be noticed that $| T_A^0 >$ and $| T_A^* >$ have exactly the same spin densities; there is thus no spin polarization.

The total wavefunctions of the two-molecule system are built as follows:

$$\begin{aligned} | SS > &= | S_A S_B > \\ | ST > &= \left(| S_A T_B > \pm | T_A S_B > \right) / \sqrt{2} \\ | TT > &= | T_A T_B > \end{aligned} \tag{8}$$

$|\ >$ denotes the spin-coupled states, built as eigenvectors of the total spinoperator. At this approximation level, the two symmetrized $| ST >$ states are degenerate and the spin states $| TT >$ too. γ is calculated in accordance of eq.3, with:

$$E_{XY} = \left\langle XY \left| \hat{H} \right| XY \right\rangle \qquad X, Y = L, H \tag{9}$$

$\hat{H}$ being the total Hamiltonian. Omitting the exchange and overlap integrals between the orbitals of two different molecules, γ takes the form:

$$\gamma = \gamma^{(0)} + \gamma^{(1)} \qquad \text{with}$$

$$\gamma^{(0)} = j - \frac{j_1 + j_2}{2} \qquad \text{and} \qquad \gamma^{(1)} = 4 \frac{(j_{\pi 1}^0 - j_{\pi 2}^0)\,(j_{\pi 1} - j_{\pi 2})}{F_{\pi^*} - F_\pi} \tag{10}$$

$$j = \left\langle a_1(1)\, b_2(2) \left| \frac{1}{r_{12}} \right| a_1(1)\, b_2(2) \right\rangle \tag{11}$$

$$j_k = \left\langle a_k(1)\, b_k(2) \left| \frac{1}{r_{12}} \right| a_k(1)\, b_k(2) \right\rangle \qquad k = 1, 2 \qquad (11')$$

$$j_{\pi k} = \left\langle \pi_A(1)\, b_k(2) \left| \frac{1}{r_{12}} \right| \pi_A^*(1)\, b_k(2) \right\rangle \qquad k = 1, 2 \qquad (11'')$$

It can be shown that the zeroth-order term, $\gamma^{(0)}$, is negative. This term, however, is quite small, because the Coulomb integrals are weak, due to the large distance between the metal centers, and that the j, j_1 and j_2 values are very close to each other. It means that the direct interaction between the metal centers has a weak "anticooperative" effect.

The first-order term, $\gamma^{(1)}$, is positive, because $(j^0_{\pi 1} - j^0_{\pi 2})$ and $(j_{\pi 1} - j_{\pi 2})$ are of the same sign. To estimate the order of magnitude of $j^0_{\pi k}$ and $j_{\pi k}$, we may plot the overlap density $\pi_A.\pi_A^*$. In fact, we have determined the overlap densities $\pi.\pi^*$ of the isolated ligand, since π_A and π_A^* are very close to ligand orbitals. Figure 4 shows two π molecular orbitals of bipyridine, calculated with the extended Hückel method. The former, noted π^*, is the LUMO; the latter, noted π, is slightly below the HOMO. These molecular orbitals have been chosen because they have both large contributions on the coordinating nitrogen atoms. Figure 5 represents the $\pi.\pi^*$ overlap density.

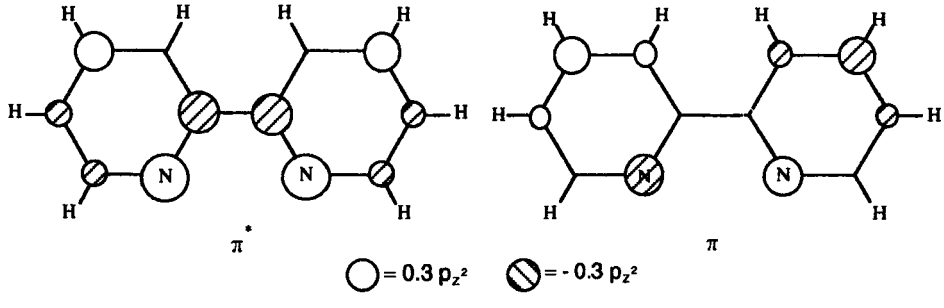

FIGURE 4 Two molecular orbitals of bipyridine.

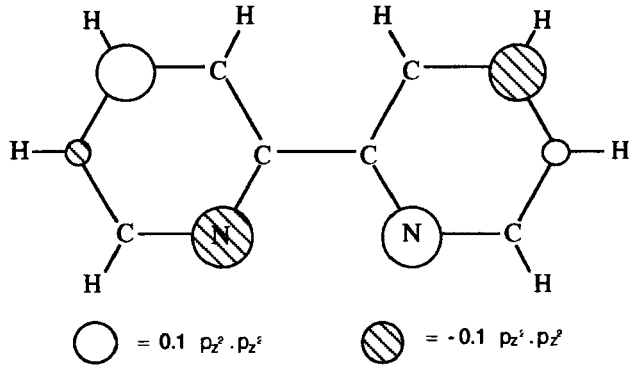

FIGURE 5 Overlap density between the molecular orbitals π^* and π of bipyridine, calculated with the extended Hückel method

The overlap density on the nitrogen atoms is comparable to the values of the charge density of the corresponding orbitals. $j^0_{\pi k}$ (eq.7) is an intramolecular ionic integral involving a metal charge density and this overlap density. It must be of the same order of magnitude than a Coulomb integral and is thus quite large. $j_{\pi k}$ (eq.11") is an intermolecular ionic integral, whose main contribution is due to the delocalization of b_k on the π ring. Thus, $\gamma^{(1)}$ must be larger than $\gamma^{(0)}$.

This model can be easy improved, with several ligand orbitals, and five quasi-degenerate metal orbitals.

CONCLUSION

The orbital model we proposed in this paper shows that an orbital interaction, namely the Coulomb repulsion of the electronic clouds of the two molecules, may be a microscopic origin of the cooperativity. It predicts a competition between the direct interaction between the metal centers and the indirect one through the ligands. The former leads to anticooperativity, whereas the latter, which in general dominates, leads to cooperativity.

Numerical evaluations of $\gamma^{(0)}$ and $\gamma^{(1)}$ in above mentioned compounds are in progress, to compare them to the Γ value extracted from the experimental data.

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