On the Mechanism of Bistability in Molecule-Based Magnets: the Prototype PDTA Case

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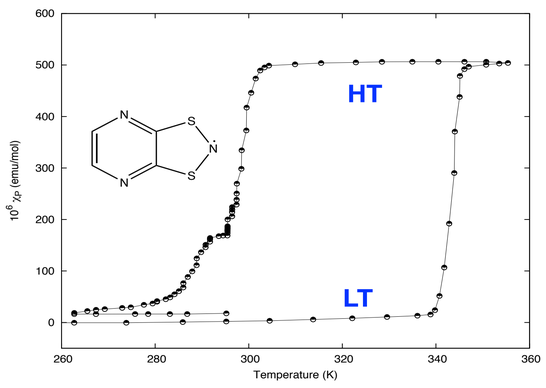
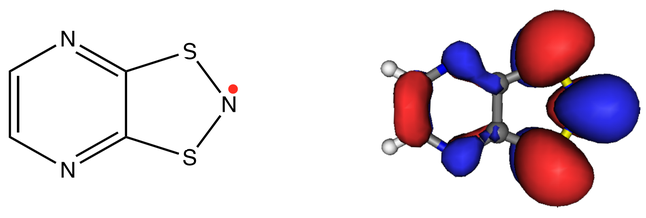
1. Introduction

The key potential property for the development of new devices, notably in data storage, light or heat sensors, is **Bistability**. Dynamical systems, like PDTA[1], presents *two stable equilibrium states* (see below the susceptibility curve as a function of T). The *coexistence* of two different crystal phases, **HT** and **LT**, within a given range of T is evident.



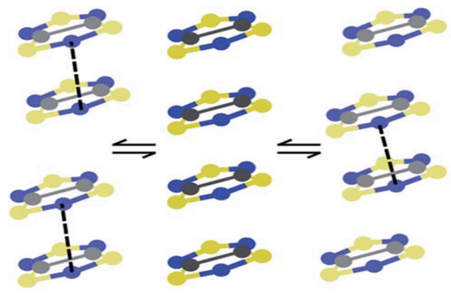
The **PDTA** crystal belongs to the DTA family[1]. These systems present the same ···-S-N•-S-··· moiety, where the *nitrogen* atom *formally* hosts the unpaired electron.



Structural Formula **SOMO**

PDTA
[1,3,2]-pyrazinodithiazol-2-yl

The **Fast Pair-Exchange Dynamics** has been observed in TTTA[2,3], for which the regular π-stacks of the HT polymorph (in the **center** of the picture below), result from the dynamic interconversion between two distorted stacks, in **left** and **right-hand** side.



This **Fast Pair-Exchange Dynamics** might also affect both the *phase transition* (**LT** –>**HT**) and the *magnetic response* of the PDTA material at **HT**.

5. Conclusions

In this work we used the "First-Principles Bottom-Up" strategy, for studying the **LT** and **HT** phases of the PDTA. We were able to:

- determine which radical pairs play an important role in the structural and magnetic description of PDTA system;
- correctly reproduce the DIAMAGNETIC and PARAMAGNETIC behavior of **LT** and **HT** phases of PDTA, respectively;
- correlate numerical differences in the **HT** simulated curves with thermal fluctuations.

FUTURE WORK:

1. perform the "DYNAMICAL" analysis of PDTA system, for both **LT** and **HT** phases;
2. assess if PDTA undergoes Fast Pair-Exchange Dynamics, as TTTA.

2. Objectives

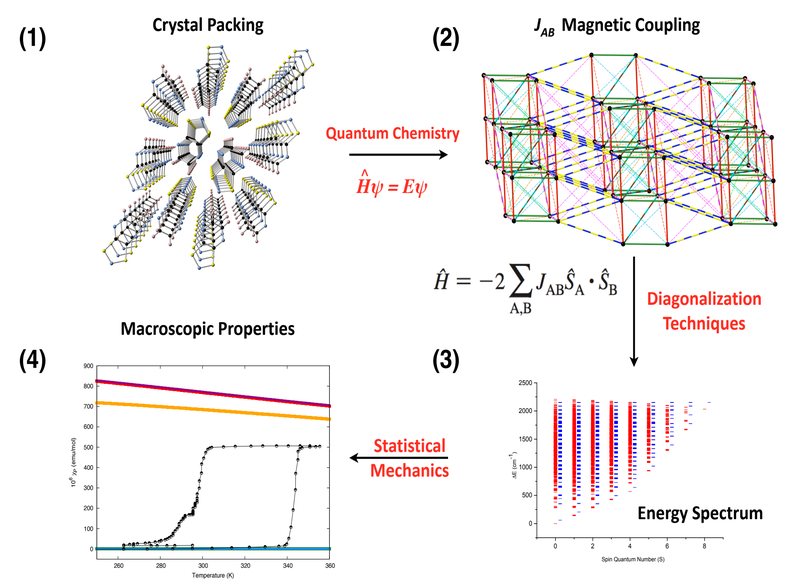
On the basis of the work carried out by *Vela et al.*[2,3], we want to:

- evaluate the *nature* of the phase transition from **LT** –> **HT** in the PDTA material;
- check whether the *Vibrational Entropy* for the **HT** phase of PDTA plays a *key role* in the phase transition;
- assess whether the **HT** phase of PDTA undergoes *Fast Pair-Exchange Dynamics*.

3. Methodological Details

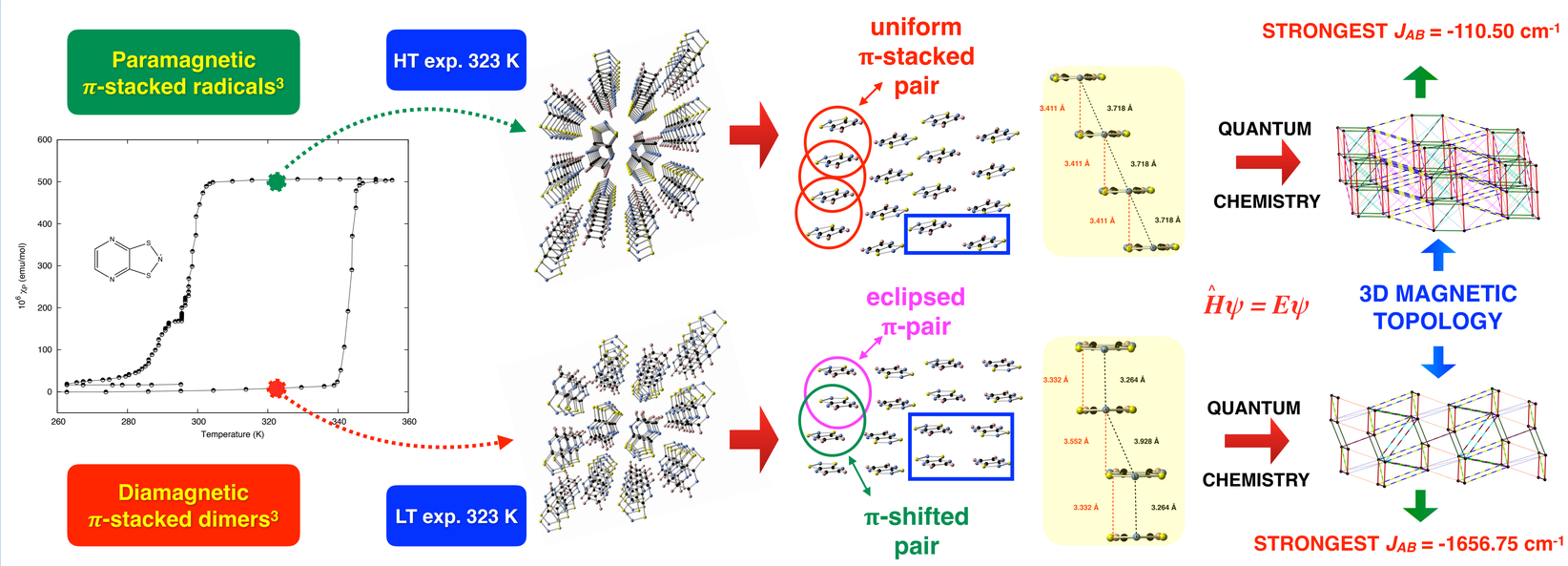
The correct description of the magnetic properties of DTA-based materials can be performed from a "STATIC" and "DYNAMICAL" points of view. The "STATIC" analysis is based on the **First-Principles Bottom-Up**[4], which is a 4 steps procedure:

- **STEP (1):** Analysis of the ***experimental*** crystal packing in order to identify all the unique **radical**···**radical** pairs;
- **STEP (2):** Calculation of each magnetic interaction, J_{AB}, between each unique **radical**···**radical** pairs, using the Heisenberg-Hamiltonian $\hat{H} = -2J_{AB} \cdot \hat{S}_A \cdot \hat{S}_B$;
- **STEP (3):** Determination of the magnetic topology of the crystal described by *non-negligible* J_{AB};
- **STEP (4):** Calculation of the macroscopic magnetic properties (χ, χT, ...) and comparison with the experimental data.



The "DYNAMICAL" approach takes into account the role of *thermal fluctuations* to study both the crystal structure and the magnetic properties.

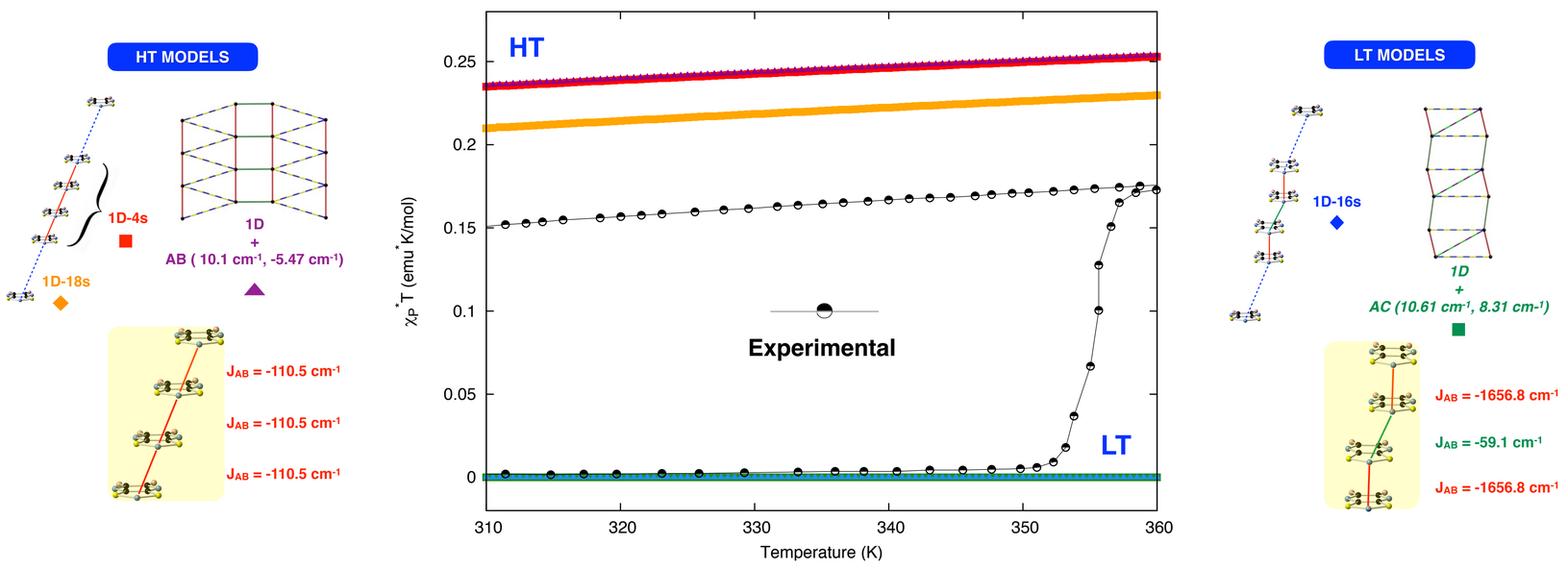
4. Results & Discussion: The Static Analysis of PDTA



(1) Analysis of the experimental crystalline structure of the compound and definition of each unique pair.

(2) Calculation of each J_{AB} by means of the *BS* approximation, as $J_{AB} = E^S_{BS} - E^T$, at **DFT** level.

(3) Definition of the **magnetic topology** of the crystal in terms of *non-negligible* J_{AB} interactions.



(4) Calculation of magnetic susceptibility curves using 1D and 2D magnetic models for **LT** and **HT** phases, and direct comparison with experimental data.

6. References

(1) Brusso, J. L. et al., *JACS* **(2004)**, 126, 8256.
(2) Vela, S. et al., *Nature communications* **(2014)**, 5.
(3) Vela, S. et al., *Chem. Sci.*, **(2015)**, 6, 2371.
(4) Deumal, M. et al., *J. Phys. Chem. A* **(2002)**, 106, 1299

7. Acknowledgments

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