Computational Analysis of Interface Propagation in a Switchable Cooperative Fe(III) Spin-Crossover Material

David Ndrio,[a] Francesc Viñes,[a] Adriá Gil[b]

a, Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona francesc.vines@ub.edu. c/ Martí i Franquès, 1-11, 08028, Barcelona, Spain.

b, Universitat de Lleida, Departament de Química, Física i Ciències Ambientals i del Sòl, ETSEAFIV – Escola Tècnica Superior d'Enginyeria Agroalimentària i Forestal i de Veterinària, Lleida, Spain. adria.gil@udl.cat. Av. Alcalde Rovira Roure, 191, 25198, Lleida, Catalonia, Spain.

david.ndrio@ub.edu

Introduction

Spin-crossover (SCO) refers to the reversible switching between a material's **low-spin** (LS) and **high-spin** (HS) states in response to external factors, such as changes in temperature, pressure, or light.[1] This phenomenon initiates at specific sites (surfaces or defects), and propagates throughout the material via **intermolecular interactions**.[2] Therein, understanding this behavior is fundamental for the comprehension of the characteristics of the LS/HS interface propagation.

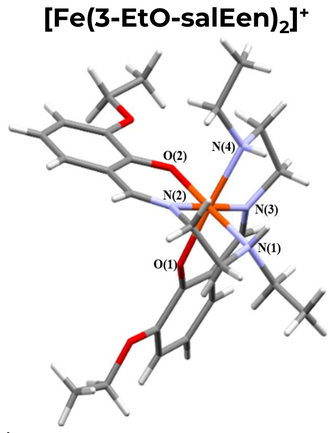
SCO materials have attracted attention due their potential applications in sensors, artificial muscles, energy harvesting, and smart materials.[3] While this phenomenon has been extensively studied and documented for Fe(II) complexes, the research of this behavior in **Fe(III)** materials is yet **limited**. In this study, we report the observation of interface propagation in a Fe(III) SCO material, specifically in the compound **$[Fe(3\text{-EtO-salEen})_2]NO_3$**.

Computational Details

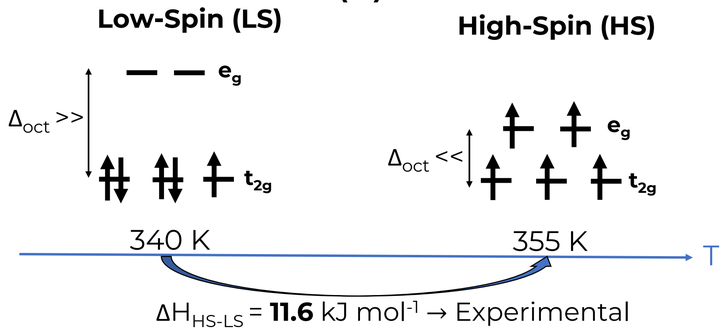
- **Density Functional Theory** (DFT) calculations, using the Vienna *Ab Initio* Simulation Package (**VASP**) software [4], employing periodic boundary conditions.
- Projector Augmented Wave (**PAW**) **pseudopotentials** for core electron density [5], and a **415 eV** kinetic energy cutoff for the plane waves used to define the valence electron density.
- Gaussian smearing (**0.2 eV**) [6], with final total energy extrapolated to zero smearing.
- **K**-points: Only Γ point in a Monkhorst-Pack scheme [7], with no **k**-points mesh shift.[8]

Spin-Crossover in the Fe(III) Complex

$[Fe(3\text{-EtO-salEen})_2]^+$



Fe(III) → d^5

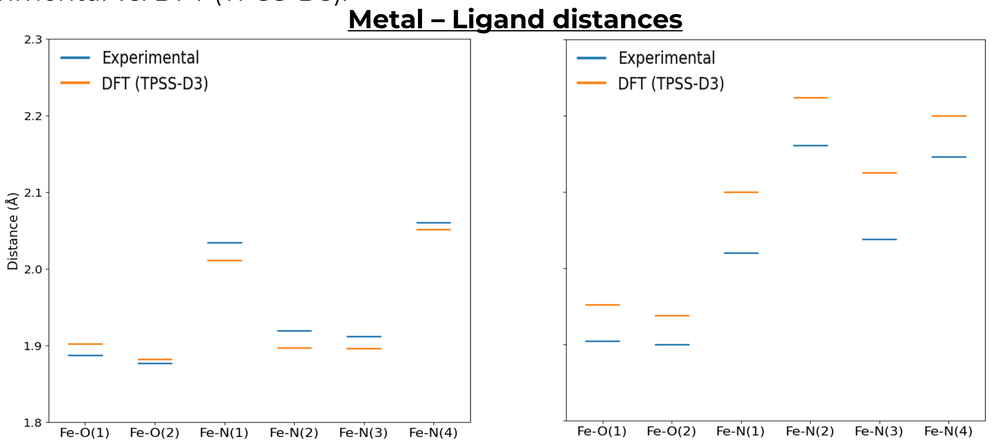


- **TPSS-D3** [9, 10] functional reproduces well the experimental enthalpy:
  ΔE_{HS-LS} (TPSS-D3)= 11.1 kJ mol^{-1} ✓

Geometrical Parameters

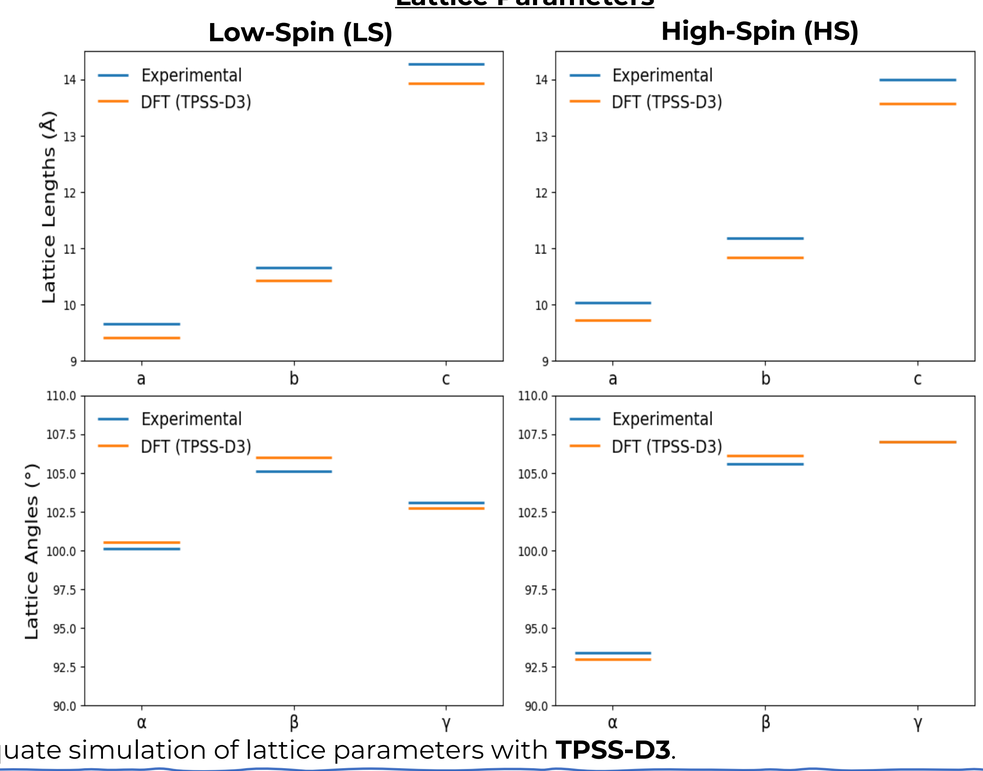
- Experimental vs. DFT (TPSS-D3):

Metal – Ligand distances



- Computational results with TPSS-D3 **reproduce correctly** experimental geometrical parameters.
- HS configuration differences are slightly larger due to the HS experimental geometry not being 100 % pure (mix with LS configuration).

Lattice Parameters

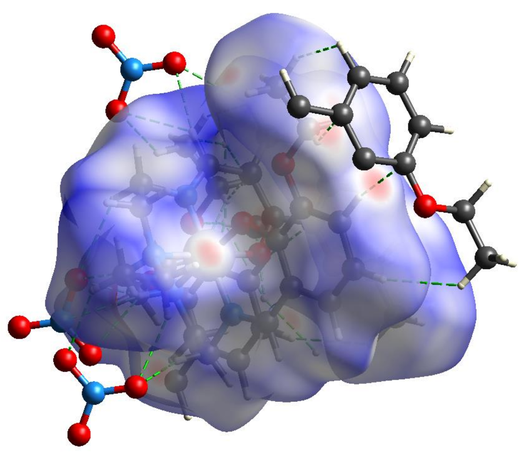


- Adequate simulation of lattice parameters with **TPSS-D3**.

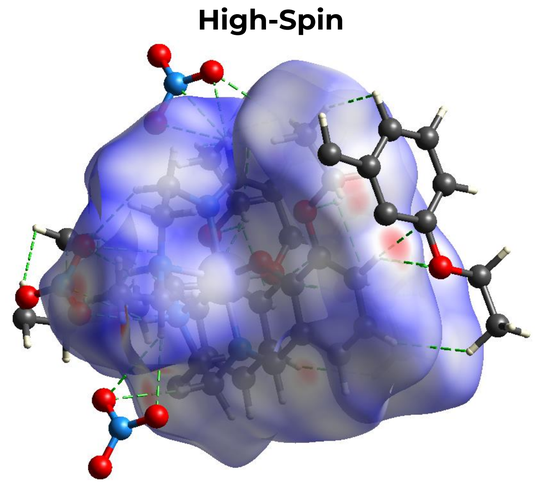
Intermolecular Interactions Analysis

- **Hirshfeld Surfaces**:

Low-Spin

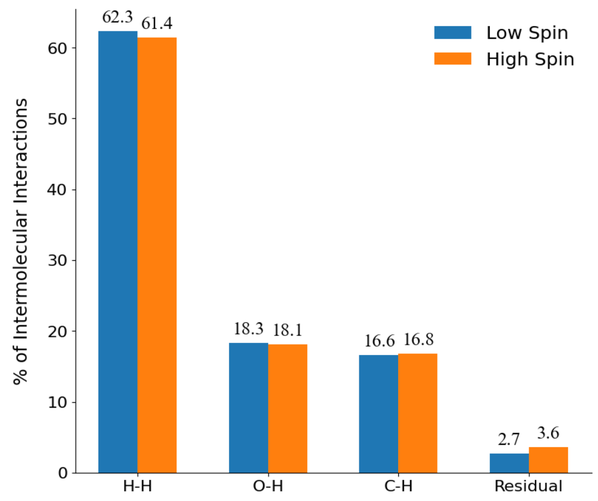


High-Spin



- Close contact regions, for both configurations, with:
  - **O···H** interactions involving both the O from NO_3^- and from the EtO group (acceptor), and H bonded to either C (in C-H) or N (in N-H) as the donor.
  - **π···H** interactions involving the aromatic rings (both donor and acceptor).

Intermolecular Interactions (TPSS-D3)



- **H···H** interactions are the **largest contributor** in both configurations, despite their weak nature.
- The second largest contributions in both cases arise from **stronger O···H** interactions, followed by **C···H** interactions.
- A slight **reduction** in **H···H** and **O···H** interactions is produced in the transition to the HS state.
- **C···H** interactions exhibit a **slight increase**, while residual (**C···C**, **C···O** and **N···H**) contributions show a more **significant growth**.

Conclusions

- The functional **TPSS-D3** accurately predicts the energy of spin transition (**ΔE_{HS-LS}**) and simulates well the geometric parameters of the studied complex.
- Hirshfeld surface analysis reveals that, while **H···H** interactions are the largest contributor to the intermoleuclar forces, the **strongest** and most significant are **O···H** interactions, likely responsible for the **high cooperativity** observed in this system.
- The surfaces also reveal important **π···H** interactions present in both LS and HS configurations.
- During the spin transition to the HS state, although there are no substantial variations in the overall interaction profile, the contributions of both **H···H** and **O···H** interactions **slightly decreased**. On the other hand, a more noticeable **increase** in the percentage of **residual** interactions has been observed, indicating a shift in the balance of forces in the HS state.

Bibliography

[1] O. Sato, J. Tao, Y. Z. Zhang, *Angew. Chem. Int. Ed.* **2007**, *46*, 2152-2187.
[2] M. G. Reeves, E. Tailleur et al. *Chem. Sci.* **2021**, *12*, 1007-1015.
[3] A. Enriquez-Cabrera, et al. *Coordination Chemistry Reviews*. **2020**, *419*, 213396.
[4] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169-11186.
[5] J. Hafner, *J. Comput. Chem.* **2008**, *29*, 2044-2078.
[6] J. J. Jorgensen, G. L. W. Hart, *Model. Simul. Mater. Sci. Eng.* **2021**, *29*.
[7] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188-5192.
[8] P. Kratzer, J. Neugebauer, *Front. Chem.* **2019**, *7*, 106.
[9] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.
[10] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

ACKNOWLEDGMENTS

MICIU/AEI/10.13039/501100011033
PID2021-126076NB-I00
TED2021-129506B-C22
CEX2021-001202-M
Ac2216561
2021-SGR-00079