

Computational Modeling of Spin-Crossover systems: From molecules to Crystals

J.Cirera^[1]

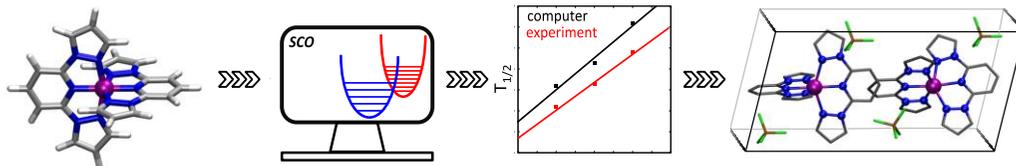
¹Departament de Química Inorgànica i Orgànica and Institut de Recerca de Química Teòrica i Computacional, Universitat de Barcelona, Diagonal 645, Barcelona 08028, Spain, jordi.cirera@qi.ub.es

Due to their inherent technological applications as molecular level switches, Spin-Crossover systems (SCO) are the focus of intense research both in chemistry. SCO molecules display two alternative electronic states with similar energies accessible by means of an external stimulus, most commonly the temperature, which grants access to the manipulation of an electronic structure property using a macroscopic perturbation. However, designing SCO systems that undergo the transition at specific conditions is a difficult problem

In this presentation, the use of electronic structure methods at the Density Functional Theory (DFT) level to compute the transition temperature ($T_{1/2}$), a key physical parameter in the characterization of such systems, will be outlined.^[1] A proper benchmarking of different DFT methods to compute spin-state energies for first row transition metal systems (d^4 to d^7) will be presented. This computational approach allows us to understand the experimental trends observed on $T_{1/2}$ for several families of SCO systems in terms of their underlying electronic structure. Our methodology has been able to explain the origin of the SCO phenomena in organometallic complexes such as the $[\text{Mn}(\text{Cp}^R)_2]$ ($R = \text{Me}$, ^iPr or ^tBu) and $[\text{Cr}(\text{indenyl})_2]$,^[2,3] as well as other unusual systems, such as low-coordinated Fe(II) complexes.^[4,5]

Finally, an expansion of the presented methodology to account for crystal packing effects will be presented. Using a specifically calibrated DFT-U method, accurate spin-state energies for Fe^{II} and Fe^{III} SCO systems can be computed at the solid state, in excellent agreement with experimental thermochemical data.^[6]

The presented results validate the use of DFT methods not only to model experimentally reported systems, but also to explore the virtual screening of new SCO systems using computational tools



References:

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