

ELECTRONIC-STRUCTURAL INTERPLAY IN SPIN CROSSOVER MOLECULAR COMPLEXES UNDER PRESSURE

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Spin crossover (SCO) is typically described, in the simplest cases, as a two-state electronic equilibrium between a high and a low-spin state. In this context, temperature and pressure are often considered equivalent thermodynamic variables capable of shifting the same fundamental equilibrium. However, in the solid state, the spin transition is inherently coupled to a deformable and cooperative lattice, whose collective response may affect not only the transition conditions, but also the transformation pathway.

Among the most commonly studied SCO compounds are those based on Fe(II) ions (d^6) in an octahedral coordination sphere, which commonly switch between two distinct spin states: high-spin (HS, $S = 2$) and low-spin (LS, $S = 0$). These SCO materials have been proposed as potential candidates for solid-state refrigeration applications since some of them have evidenced large to colossal barocaloric effects. In this regard, the interest in studying (p,T) phase diagrams in these systems and unravel their behaviour under pressure has strongly increased.

In this contribution, we examine a series of Fe(II) complexes that display contrasting pressure–temperature behaviour. By exploring different systems, we show that the structural topology plays a decisive role in how the electronic transition unfolds under pressure. In this regard, the lattice may evolve cooperatively with the spin switching, or undergo phase transitions in order to accommodate pressure, allowing accessing structural rearrangements that are not observed along the thermal pathway.

A combination of high-pressure Raman spectroscopy, XANES, and single-crystal and powder X-ray diffraction allowed us to analyse how electronic and structural degrees of freedom interact upon compression. Our findings highlight the ability of pressure to uncover lattice instabilities and alternative transformation routes, and further emphasise that SCO in molecular solids reflects the interplay between electronic states and collective structural response.