UNDERSTANDING KINETICALLY CONTROLLED SPIN TRANSITIONS IN BISTABLE SPIN CROSSOVER MATERIALS

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The performance of spin-crossover (SCO) transition is often evaluated with its two characteristic temperatures; $T_{1/2}$ describes the *thermally driven* spin transition occurs, and T_{LIESST} describes the thermal relaxation of the kinetically-trapped metastable state. Beyond empirical trends (e.g. the Bordeaux relationship), the fundamental reason dictating $T_{1/2}$ and T_{LIESST} lies in the temperature evolution of the Free Energy Surfaces (FESs) of the relevant electronic states (HS and LS). These ultimately dictate the thermodynamic and kinetic feasibility of the two spin transitions. Particularly key are the energies of the HS and LS minima, and those of the barriers connecting these states either directly (HS-LS), or indirectly through the intermediate triplet state (HS-IS-LS). From the perspective of atomistic computational modelling, $T_{1/2}$ is typically evaluated by computing LS/HS minima and adding vibrational corrections at stationary points.[ref] However, this *thermodynamic* picture neglects kinetics, so energy barriers are not evaluated, and the T_{LIESST} cannot be predicted and rationalised.

In a recent manuscript, we addressed this gap by explicitly incorporating kinetics into the SCO description.[1] For the benchmark $[Fe^{II}(1\text{-bpp})_2]^{2+}$, **1**), we reconstructed their temperature-dependent FESs, and located the Minimum Energy Crossing Points (MECPs) connecting the two minima. This enabled us to estimate the 'reaction' barriers, temperature dependent rate constants, and half-life times using a Transition State Theory-like treatment adapted for spin-forbidden processes.

Our protocol combined ab-initio computations and state-of-the-art machine-learning predictions to estimate $T_{1/2} \approx 254$ K and $T_{LIESST} \approx 80$ K for isolated molecules of **1**, in excellent agreement with the values obtained experimentally for salts based on this complex (≈260 K and ≈81 K, respectively). Also, we discovered that the thermal LS→HS transition is thermodynamically controlled (as expected), yet it only becomes kinetically accessible above *ca.* 130 K, which might explain the absence of SCO systems with $T_{1/2}$ below this temperature. Finally, we found that LIESST thermal relaxation happens through the direct HS→LS mechanism, in contrast with the ultrafast LIESST relaxation after photo-excitation, for which experiments have unveiled the participation of the IS state (LS* -> IS > HS).

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[1] S. Vela, M. Fumanal, C. Sousa, *J. Mater. Chem. C* **2023**, 11, 235–243.