Spin-State Control in Molecular (MOST) and Extended (MOF) Systems: From Ultrafast Photoisomerization to Spin Frustration in Catalysis

Gaurab Ganguly [1]

[1] *Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Str. 17, 1090 Vienna, Austria.*

Controlling spin states is fundamental to modulating reactivity in both molecular and extended systems, with broad implications for solar energy storage and catalysis. In this talk, I present a comparative study of two distinct yet complementary classes of materials—molecular solar thermal (MOST) systems and metal–organic frameworks (MOFs)—to demonstrate how the selection of spin states and their dynamic interconversion govern material function.

In the first part, I unravel the contrasting photochemistry of (fulvalene)$Ru_2(CO)_4$ and its Fe analogue using multireference ab initio methods and Marcus theory.[1] For Ru, excitation above 350 nm triggers ultrafast, barrierless intersystem crossing (ISC), forming a triplet biradical that drives photoisomerization, while excitation below 300 nm leads to decarbonylation. The Fe complex fails to isomerize due to a high ISC barrier in the Marcus inverted regime, suppressing triplet formation. El-Sayed's rule and spin–orbit coupling analyses explain how Ru stabilizes the triplet state to facilitate efficient energy storage.

In the second part, I shift to extended systems and investigate MIL-101(Fe), a Fe-based MOF known for gas adsorption and catalysis. Standard high-spin DFT overlooks spin frustration caused by the triangular Fe_3O node. Using broken symmetry and spin-flip DFT, I show that capturing this frustration explains the temperature-dependent adsorption behavior, governing N_2 fixation at ambient conditions and CO binding at elevated temperatures.[2]

Together, these case studies highlight the critical role of accurate spin-state modeling in understanding reactive pathways across molecular and extended systems.

---

[1] Lomont. J. P. *et al. Acc. Chem. Res.* **2014**, *47*, 1634.
[2] Li, G. *et al. J. Solid State Chem.*, **2020**, *285*, 121245.