

Ab initio study of spin-crossover materials for applications in gas adsorption

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Abstract: The use of highly porous, chemically tunable solid adsorbents such as metal-organic frameworks (MOFs) has attracted much interest in the past 20 years for their potential application in gas separation and carbon capture technologies. In this work, we propose to computationally design MOFs whose high affinity for guest molecules can be modified under temperature treatment. With a suitable choice of ligands and metal centers, MOFs exhibiting a thermally-induced spin crossover (SCO) and a concomitant change in the adsorption properties can be developed to possibly yield more energy-efficient gas capture-and-release.

From a computational point of view, the challenge in simulating the SCO phenomenon using *ab initio* electronic structure methods is represented by the evaluation of the thermodynamics of SCO. To address this issue, we develop a DFT+U-based scheme to achieve an accurate description of spin-state energy differences in Fe(II) complexes. A critical assessment of the Hubbard U approach in the description of spin-state energetics is presented and insights from this analysis are used to propose a practical and efficient way to overcome them. This approach, which is tested and validated against experiments and coupled cluster-corrected CASPT2 results, is then used to propose the proof-of-concept *in silico* of temperature-induced SCO-MOF for efficient gas release.