Ab initio study of cyanide photo-dissociation/-association in a single crystal

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ABSTRACT

Comprehension and control of light-induced processes in condensed phases remain amongst the greatest challenges in material science.[1] In this work, we use periodic spin-polarized DFT to replicate and analyze such phenomena in the single-crystal of $K_4[Mo^{III}(CN)_7]\cdot 2H_2O$. For this compound, we experimentally confirmed the photodissociation of the cyanide ligand resulting in the change of metallic complex geometry from a 7-coordinate capped trigonal prism to a 6-coordinate octahedron (Fig. 1).[2] Such transformation is accompanied by the spin-state alteration of the Mo^{III} center between $S = 1/2$ and $S = 3/2$. The structural change can be fully reversed by the red-light irradiation, which leads to the re-association of the cyanide ligand and a complete recovery of the initial state. To study and replicate the properties of $K_4[Mo^{III}(CN)_7]\cdot 2H_2O$ in both spin states we used several density functionals as well as multiple optimization strategies. Spin-state locking protocol was used to enforce the structural transformations *in silico*. The presented results are a significant step towards the discovery of photo-switchable high-temperature magnets and nanomagnets.

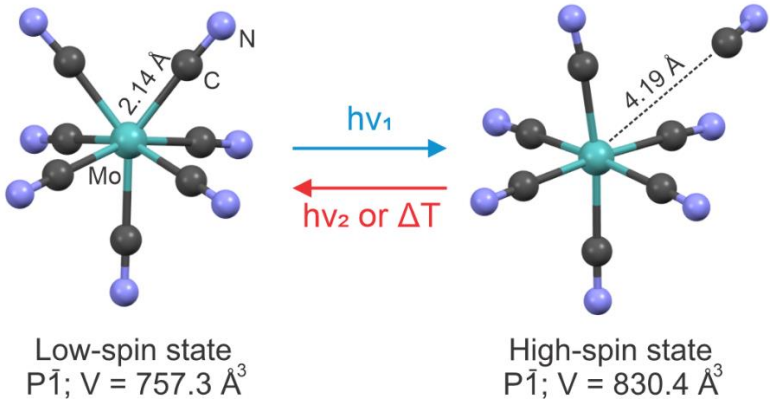

Fig 1 : Light-induced CN^- dissociation/association in $K_4[Mo^{III}(CN)_7]\cdot 2H_2O$.

References

[1] Thaggard, G.C.; Haimerl, J. et al. *J. Am. Chem. Soc.* **2022**, *144*, 23249-23263.

[2] Magott, M.; Arczyński, M.; Malec, L.M. et al. **2024** (in preparation).