

Ultrafast Intersystem Crossing in Third-Row and Fifth-Row Transition Metal Complexes

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Intersystem crossing (ISC) in transition metal complexes is very different from ISC in typical organic molecules. This is due to the electronic structure of these complexes that lead to a high density of excited electronic states as well as very large spin-orbit couplings due to the high nuclear charge of the metal center. Here, we compare the ultrafast ISC mechanism of two prototypical transition metal complexes, the third-row complex $[\text{Fe}(\text{CN})_4(2,2'\text{-bipyridine})]^{2-}$ and the fifth-row complex $[\text{Re}(\text{CO})_3(\text{imidazole})(\text{phenanthroline})]^+$. Both complexes have been assigned ISC on a 100 fs time scale by ultrafast spectroscopy in aqueous solution.[1, 2] However, considering the nuclear charge of the two metals, the Re complex should exhibit significantly faster ISC than the Fe complex. By extensive simulations using the Surface Hopping including Arbitrary Couplings (SHARC) [3] method, we show that indeed the ISC mechanisms of these two complexes are different. Most prominently, we provide evidence that ISC in the Re complex can be clearly separated into electronic ISC and nuclear-relaxation-driven ISC, whereas in the Fe complex electronic and nuclear effects cannot be separated.

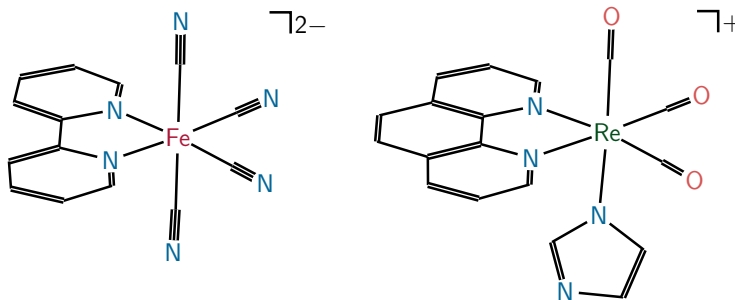


Figure 1: Chemical structures of $[\text{Fe}(\text{CN})_4(2,2'\text{-bipyridine})]^{2-}$ and $[\text{Re}(\text{CO})_3(\text{imidazole})(\text{phenanthroline})]^+$.

References

- [1] W. Zhang et. al.: *Chem. Sci.* (2017), **8**, 515.
- [2] A. El Nahhas et. al.: *Inorg. Chem.* (2011), **50**, 2932.
- [3] S. Mai et. al.: *WIREs Comput. Mol. Sci.* (2018), **8**, e1370.