

## Orbital-specific mapping of chemical dynamics with x-rays

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Charge and spin density changes at the metal sites of transition-metal complexes and in metalloproteins determine reactivity and selectivity. To understand their function and to optimize complexes for photocatalytic applications the changes of charge and spin densities need to be mapped and ultimately controlled.

We used atom- and orbital-specific [1] x-ray free-electron laser spectroscopy and quantum chemical theory [2] to map the chemical dynamics of an iron-centered complex in solution on the femtosecond time scale [3]. Resonant inelastic x-ray scattering (RIXS) at the Fe L-edge is used to probe the frontier-orbital interactions locally at the Fe site. Spin crossover and ligation are found to define the excited-state dynamics.

It is demonstrated how correlating orbital symmetry and orbital interactions with spin multiplicity allows for determining the reactivity of short-lived reaction intermediates. I will discuss how this complements approaches that probe structural dynamics and how it can be extended [4] to map the local chemical interactions and their dynamical evolution in metalloproteins.

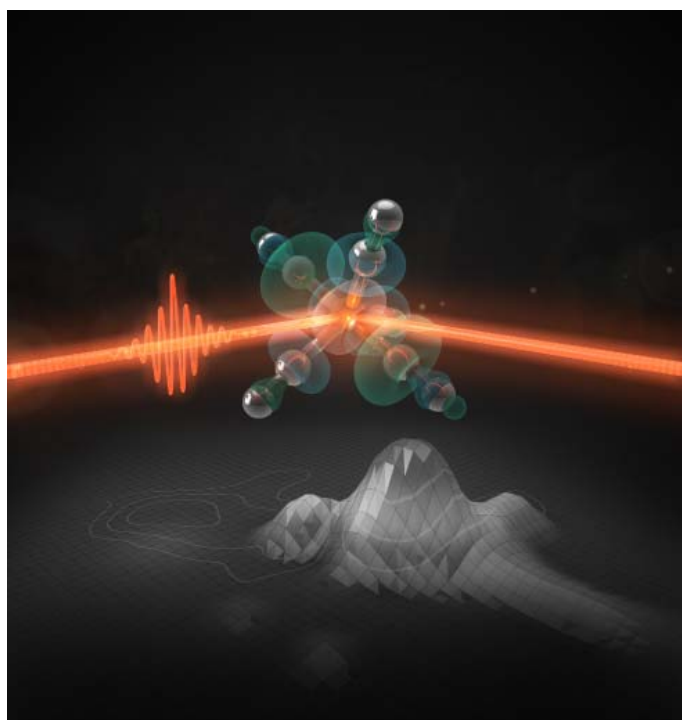


Figure 1: Orbital-specific mapping of chemical dynamics at the metal center of a transition-metal complex with ultrafast x-rays

### References

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- [4] R. Mitzner et al. *J. Phys. Chem. Lett.* **4**, 3641 (2013).

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