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Orbital-specific mapping of chemical dynamics with ultrafast 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. I will discuss how time-resolved soft x-ray spectroscopy enables a fundamental understanding of local atomic and intermolecular interactions and their dynamics on atomic length and time scales of Ångströms and femtoseconds. The approach consists in using time-resolved, atom- and orbital-specific x-ray spectroscopy and quantum chemical theory to map the frontier-orbital interactions and their evolution in real time of ultrafast chemical transformations. We recently used femtosecond resonant inelastic x-ray scattering (RIXS, the x-ray analog of resonant Raman scattering) at the x-ray free-electron laser LINAC Coherent Light Source (LCLS, Stanford, USA) to probe the reaction dynamics of a transition-metal complex in solution on the femtosecond time scale. 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 to map the local chemical interactions and their dynamical evolution in metalloproteins.