Chemical interactions and dynamics in photosystem II and metal complexes from x-ray spectroscopy

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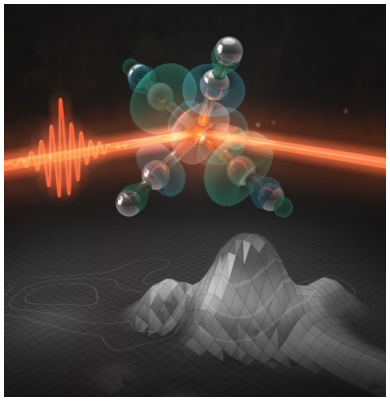
Charge and spin density changes at the metal site of transition-metal complexes and in metalloproteins determine reactivity and selectivity. To understand the function of metalloproteins and to optimize complexes for photocatalytic applications such as hydrogen production or selective carbon-hydrogen bond activation the changes of charge and spin densities need to be mapped and ultimately controlled. The local chemistry in metalloproteins and a molecular-level understanding of how transition-metal complexes catalyze reactions, however, is still scarce because suitable methods for detailed characterization of atom-specific frontier-orbital interactions in metalloproteins and in molecular electronic excited states have been largely lacking.



X-ray spectroscopy at free-electron lasers enables a new class of experiments for mapping chemical interactions and their dynamics. I will present an application of time-resolved and element-specific x-ray spectroscopy at the x-ray free-electron laser Linac Coherent Light Source LCLS in Stanford (USA) to resolve the excited-state behavior of a metal complex in solution [1] and I will outline a strategy to extend this with the goal to map the local chemical interactions and their dynamical evolution in metalloproteins [2].

This novel approach is enabled by the ability to probe frontier-orbital interactions with atom and orbital specificity. It is expected to be broadly applicable in the chemical sciences and in the investigation of metalloproteins, and it complements approaches that probe structural dynamics.

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[2] R. Mitzner, J. Rehanek, J. Kern, S. Gul, J. Hattne, T. Taguchi, R. Alonso-Mori, R. Tran, C. Weniger, H. Schröder, W. Quevedo, H. Laksmono, R. G. Sierra, G. Han, B. Lassalle-Kaiser, S. Koroidov, K. Kubicek, S. Schreck, K. Kunnus, M. Brzhezinskaya, A. Firsov, M. P. Minitti, J. J. Turner, S. Moeller, N. K. Sauter, M. J. Bogan, D. Nordlund, W. F. Schlotter, J. Messinger, A. Borovik, S. Techert, F. M. F. de Groot, A. Föhlisch, A. Erko, U. Bergmann, V. K. Yachandra, Ph. Wernet, J. Yano. L-edge X-ray Absorption Spectroscopy of Dilute Systems Relevant to Metalloproteins Using a X-ray Free-Electron Laser, *J. Phys. Chem. Lett.* **4**, 3641 (2013).