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Ligand dissociation and recombination of Nitrosyl-myoglobin in physiological media studied by ultrafast X-ray spectroscopy and X-ray Diffuse Scattering

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Myoglobin is a small protein consisting of a single polypeptide chain of 153 amino acid residues and a heme as its active center. It plays a central role in many biological functions based on detection, transport, release and/or binding of molecular ligands such as O2, CO, NO, CN, etc. The unligated high-spin form (deoxyMb) binds the ligand at the Fe of the heme, leading to a change to the planar low-spin ligated form, which is the origin of the respiratory Tense (T) to Relaxed (R) state of the protein. Since, the latter is invariant, it seems ligation causes differences in spin, electronic configuration and geometric structure that determine the role of each ligand.
Nitrosyl-Myoglobin (MbNO), in particular, is not entirely understood despite its biological relevance as it controls various neurophysiological responses. The ultrafast photodissociation of low spin, planar MbNO leads to the high-spin deoxyMb. However, part of the population undergoes recombination on multiple timescales (from sub-ps to 100s ps) and formation of a high-spin domed ligated MbNO is accepted as one of the intermediates on the way back to the planar form. Previous X-ray absorption studies with 70 ps resolution(1) supported the latter hypothesis, but the nature of the earlier time kinetics is unclear. In particular, is the relaxation back to planar a cascade via spin states or is it due to steric hindrances? In order to elucidate these aspects, we combined femtosecond Fe K-edge X-ray absorption spectroscopy (XAS) with X-ray emission spectroscopy (XES) and X-ray diffuse scattering (XDS) at the FXE beamline of the European-XFEL (Hamburg) and at SACLA (Japan). XAS probes the unoccupied density of states (DOS) and the local structure around the Fe atom, while XES probes the occupied DOS and the spin state of the intermediates, XDS allows to unravel structural changes of the protein structure. XAS is showing a faster rise for the electronic changes (main edge) compared to structural changes (post edge) and the evolution of the doming of the Fe over the first few ps. The XES results show a clear signature of the excited quintet state decaying. We will present our results from these measurements and cast them in the context of on-going studies of biosystems at XFELs.

(1) Silatani, M.; Lima, F. A.; Penfold, T. J.; Rittmann, J.; Reinhard, M. E.; Rittmann-Frank, H. M.; Borca, C.; Grolimund, D.; Milne, C. J.; Chergui, M. NO Binding Kinetics in Myoglobin Investigated by Picosecond Fe K-Edge Absorption Spectroscopy. Proc. Natl. Acad. Sci. 2015, 112 (42), 12922–12927.

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