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# Recombination dynamics of hemoproteins in physiological media investigated by picosecond X-ray absorption spectroscopy

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Recombination dynamics of hemoproteins in physiological media investigated by picosecond X-ray absorption spectroscopy

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The small protein Myoglobin (Mb), consisting of a single polypeptide chain of 153 amino acid residues and a heme group, plays a central role in many biological processes by acting as a typical heme-based sensor for diatomic molecules either toxic (e.g. CN-) and/or crucial for survival (e.g. O2, NO). While modern crystallographic techniques make it possible to determine the global structure of the protein with almost atomic resolution, one would prefer to determine the structure of the protein in its physiologically relevant environment. In addition, the biological function and reactivity of Mb strongly depends on the electronic structure of the active site. For determining both the local geometric and the electronic structure around the active center, X-ray absorption spectroscopy (XAS) is ideal. In addition, real time changes of local geometrical and electronic structure in the early stages of a biological process in proteins can be described in detail via time-resolved X-ray Absorption Spectroscopy (XAS).

Here we show our characterisation of the Fe K-edge X-ray absorption spectra of ligated (NO, O2, CN, CO) and unligated Mb (metMb, deoxyMb) [1, 2], Then using our high-repetition rate picosecond laser pump/X-ray probe setup [3] we follow the ligand recombination dynamics in MbNO under physiological conditions (pH=7, low concentration, continuously flowing of sample). Our results show, in agreement with literature that the transient spectrum of MbNO (pumped at the Q-band) consists of a long lived deligated structure identical to the deoxyMb ground state and an additional shorter-lived species. Slight deviations of the transient at 50 ps from the static difference spectrum of deoxyMb-MbNO in the post-edges features indicates the presence of NO in the vicinity of Fe. Likewise, minor deviations in the pre-edge region suggests the interaction between the NO ligand and the Fe center. Using multiple scattering, quantum chemistry and molecular dynamics simulations we are able to assign this transient species as a recombined MbNO, which is trapped in an excited spin state. These results confirm the time-resolved Raman experiments [4] and shine light on the structural and electronic dynamics, for which until now only recombination time scales are known [4, 5].

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[5] D. Ionascu et. al, J. Ame. Chem. Soc., 127(48):16921–16934, 2005.

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