Chemical dynamics with ultrashort optical and X-ray pulses

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The past decades have witnessed a revolution in sources of ultrashort pulses, from the optical to the X-ray spectral domain. This has given rise to novel approaches to track the evolution of chemical systems, with element-, spin- and structural sensitivity. In this talk, I will show the capabilities and the new insights that can be obtained from such approaches in the study of biological and molecular systems, and of materials.

In the case of biological systems, we have recently investigated the initial events of the respiratory function in heme proteins.\(^1\) The change of the low-spin (LS) hexacoordinated heme to the high spin (HS) pentacoordinated domed form upon ligand detachment and the reverse upon ligand binding, represents the “transition state” that ultimately drives the respiratory function. The mechanism of the ligand dissociation-recombination process has been hotly debated in the past 30 years, without reaching a unified picture. We have monitored the evolution of Myoglobin-NO (MbNO) from LS to the HS state and the reverse process upon ligand rebinding to the heme, after impulsive photodissociation of the NO ligand. We monitored the evolution of the system using femtosecond (fs) Fe Kα and Kβ non-resonant X-ray emission spectroscopy (XES), which is a powerful marker of the spin state. We show that the entire ligand dissociation-recombination cycle in MbNO is a spin cross-over followed by a reverse spin cross-over process.\(^2\) Ferric Cytochrome c is the most important electron transfer (ET) protein in humans, whose efficiency has been associated to its ruffled heme. However, in investigating ferric Cyt c using fs X-ray absorption spectroscopy and XES, we found that the heme also undergoes doming. The latter corresponds to a much more dramatic change of redox than ruffling, and therefore likelier to modulate the ET properties of the protein.\(^3\)

In large molecules, the concept of conical intersections (CI) is widely used to interpret intramolecular relaxation pathways and time scales, yet CI’s have never been directly observed. In a recent theoretical study,\(^4\) we proposed to use XAS and X-ray photoelectron spectroscopy (XPS) to specifically detect the passage via a CI, in the case of ethylenic molecules. We will present our current results aimed at nailing down CI’s in ethylenic molecules based on studies carried out at synchrotrons and X-ray free electron lasers.

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\(^1\) NO binding kinetics in myoglobin investigated by picosecond Fe-K-edge absorption spectroscopy
M. Silatani et al, Proceedings of the National Academy of Science 112 (2015) 12922-12927

\(^2\) Femtosecond X-ray emission study of the spin cross-over dynamics in heme proteins
D. Kinschel et al, Nature (under review)

\(^3\) Doming in Ferric Cytochrome c: Femtosecond X-ray Absorption and X-ray Emission Studies
C. Bacellar et al, Science (submitted)

\(^4\) Ultrafast X-ray spectroscopy of conical intersections