X-ray probing of ultraviolet photoprotection in isolated nucleobases

Date: January 9 2023, 15.00 h

Abstract: The conversion of light energy into other energy forms in molecules is the result of a concerted and ultrafast motion of electrons and nuclei. It often occurs under the breakdown of the Born-Oppenheimer approximation. This talk is about ultrafast experiments aimed at resolving the underlying molecular dynamics with x-ray probe pulses using free electron lasers.

The molecules in the center of this talk are nucleobases, which encode genetic information in life. Although possessing high UV absorption cross-sections, the associated damaging events are relatively rare. The ultrafast transfer of electronic energy into harmless vibrational energy plays a vital role as an internal photoprotection mechanism. This is accomplished via radiationless, ultrafast transitions from the initially excited ππ* state into lower-lying electronic states. We probed the nonadiabatic dynamics of the molecule by femtosecond resonant x-ray absorption spectroscopy at the oxygen K-edge, showing a sub-100 fs internal conversion out of the photoexcited state [1].

Thiolated nucleobases show an efficient and ultrafast relaxation into long-lived triplet states, contrasting with the ultrafast relaxation to the ground states observed in canonical nucleobases. The triplet channel gives rise to applications as photoinduced-cross linkers but also to problems related to its current use of thionucleobases as medication. We investigate the UV-induced dynamics of 2-thiouracil via time-resolved x-ray photoelectron spectroscopy (XPS) at the sulfur L-edge. We find a direct connection between the charge moving within the molecule and the binding energy shifts observed in the photoelectron spectrum.

Both experiments show that ultrafast soft x-rays are ideal to probe ultrafast changes in the electronic structure of molecules. We are planning to extend these studies to create a ‘molecular movie’ of the electronic dynamics in molecules.
