Prof. Markus Gühr
FLASH, DESY and Physikalische Chemie, Universität Hamburg

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.

[1] Probing ultrafast ππ*/nπ* internal conversion in organic chromophores via K-edge resonant absorption, T. J. A. Wolf, R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C. Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch and M. Gühr
Nature Communications 8, 29 (2017)

[2] Following excited-state chemical shifts in molecular ultrafast x-ray photoelectron spectroscopy
D. Mayer, F. Lever, D. Picconi, J. Metje, S. Alisauskas, F. Calegari, S. Düsterer, C. Ehlert, R. Feifel, M. Niebuhr, B. Manschwetus, M. Kuhlmann, T. Mazza, M.S. Robinson, R.J. Squibb, A. Trabattoni, M. Wallner, P. Saalfrank, T.J.A. Wolf, M. Gühr
Nature Communications 13, 198 (2022)