

# X-ray probing of nucleobase dynamics – comparing different x-ray observables

## Content

### Abstract:

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  $\pi\pi$  state into lower lying electronic states. We present an experiment probing the nonadiabatic dynamics of the molecule by femtosecond resonant x-ray absorption spectroscopy at the oxygen K-edge. This scheme is particularly sensitive to holes in the oxygen lone pair orbitals ( $n$ ), which are induced in the  $\pi\pi \rightarrow n\pi$  relaxation. We find a  $\pi\pi \rightarrow n\pi$  transition, occurring via a conical intersection in less than 100 fs after excitation [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 [2]. We find a direct connection between the charge moving within the molecule and the binding energy shifts observed in the photoelectron spectrum. The mechanism manifests itself into coherently modulated signals due to the oscillating electronic population. The XPS probing mechanism is sensitive to the local charge at the probed atom. Probing at multiple core levels allows to dynamically image molecular valence charge, moving over the molecule as a consequence of nonadiabatic dynamics.

[1] Probing ultrafast  $\pi\pi/n\pi^*$  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)

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