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Unveiling the wavelength dependent ultrafast relaxation of solvated thymidine with extreme ultraviolet time-resolved photoelectron spectroscopy and simulations

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The nucleobases photo-protection mechanism is at the heart of our genetic code stability: the electronic states produced by UV light absorption are rapidly converted to heat by internal conversion and safely dissipated to the environment before reactive pathways can occur. The precise understanding of photo-deactivation in these molecules and the involvement of potentially harmful trapping states thereof is still highly debated. To tackle this challenging problem, we performed extreme ultraviolet time-resolved photo-electron spectroscopy (XUV-TRPES) experiments and simulations of water solvated thymidine, unraveling its ultrafast relaxation. The large ionization spectral coverage of the employed TRPES apparatus[1] (with a probe pulse central frequency of about 30 eV) coupled to its high time-resolution (of about 20 fs) enabled to record the decay of excited states thymidine as well as the appearance of ground-state recovery signals in a single experiment. The involvement of the elusive $^1n\pi^*$ state, which acts as a bridging state between the initially excited $^1\pi\pi^*$ state and the ground-state is proven, while a significant role of such state as a population trap is excluded. This result is shown to be dependent upon the excitation wavelength (266 nm in the present study), which allows us to construct a comprehensive framework that reconciles seemingly contradictory spectroscopic measurements in the literature.[2-5] Support of theory (surface hopping QM/MM dynamics and on-the-fly XUV-TRPES spectroscopy simulation at the ab-initio CASSCF/CASPT2 level of theory) is key to decode and interpret the recorded spectra, and to shed new light on the nucleobases photo-relaxation mechanism.

[1] Phys. Rev. Lett., 128, 133001 (2022)
[2] Proc. Natl. Acad. Sci. USA, 104, 2, 435–440 (2007)
[3] Nat. Commun, 12, 1, 7285 (2021)
[4] J. Am. Chem. Soc., 137, 2931–2938 (2015)
[5] J. Am. Chem. Soc., 145, 3369–3381 (2023)

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