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Probing nucleobase photo protection with soft x-rays[1]

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We [1] present a new method for ultrafast spectroscopy of molecular photoexcited dynamics. The technique uses a pair of femtosecond pulses: a photoexcitation pulse initiating excited state dynamics followed by a soft x-ray (SXR) probe pulse that core ionizes certain atoms inside the molecule. We observe the Auger decay of the core hole as a function of delay between the photoexcitation and SXR pulses. The core hole decay is particularly sensitive to the local valence electrons near the core and shows new types of propensity rules, compared to dipole selection rules in SXR absorption or emission spectroscopy. We apply the delayed ultrafast x-ray Auger probing (DUXAP) method to the specific problem of nucleobase photoprotection to demonstrate its potential. The ultraviolet photoexcited $\pi\pi*$ states of nucleobases are prone to chemical reactions with neighboring bases. To avoid this, the single molecules funnel the $\pi\pi*$ population to lower lying electronic states on an ultrafast timescale under violation of the Born-Oppenheimer approximation. The new type of propensity rule, which is confirmed by Auger decay simulations, allows us to have increased sensitivity on the direct relaxation from the $\pi\pi*$ state to the vibrationally hot electronic ground state. For the nucleobase thymine, we measure a decay of the $\pi\pi*$ state and a subsequent filling of the vibrationally hot ground state in 300 fs. This work was supported by the AMOS program within the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.Portions of this research were carried out at the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory. LCLS is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. Other portions of this research were carried out at the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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