Probing ultrafast ππ*/nπ* internal conversion in organic chromophores via K-edge resonant absorption

Many photoinduced processes including photosynthesis and human vision happen in organic molecules and involve coupled femtosecond dynamics of nuclei and electrons. Organic molecules with heteroatoms often possess an important excited-state relaxation channel from an optically allowed ππ* to a dark nπ* state. The ππ*/nπ* internal conversion is difficult to investigate, as most spectroscopic methods are not exclusively sensitive to changes in the excited-state electronic structure. Here, we report achieving the required sensitivity by exploiting the element and site specificity of near-edge soft X-ray absorption spectroscopy. As a hole forms in the n orbital during ππ*/nπ* internal conversion, the absorption spectrum at the heteroatom K-edge exhibits an additional resonance. We demonstrate the concept using the nucleobase thymine at the oxygen K-edge, and unambiguously show that ππ*/nπ* internal conversion takes place within (60 +/- 30) fs. High-level-coupled cluster calculations confirm the method's impressive electronic structure sensitivity for excited-state investigations.

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