Probing Ultrafast Photodynamics in Malonaldehyde with Transient X-Ray Absorption

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Excited-state hydrogen transfer is a fundamental chemical reaction of relevance throughout chemistry and biology. Malonaldehyde (MA) is the simplest example that exhibits both ground- and excited-state intramolecular H-transfer and is the functional unit of the family of *β*-diketones. Experimental investigations of its photodynamics are limited in number and scope due to the challenges related to resolving ultrafast timescales of hydrogen transfer and non-adiabatic processes in a symmetric system as well as the instability of MA at ambient temperatures.

Here, we perform an *in silico* transient X-ray absorption spectroscopy experiment at complementary carbon and oxygen *K*-edges to probe its potential to monitor the ultrafast internal conversion dynamics in MA upon excitation to the $S_2(\pi\pi^*)$ state. This is accomplished by combining *Ab Initio* Multiple Spawning[1] simulations with property calculations at the algebraic-diagrammatic construction for the polarization propagator level.[2] Our simulations show the sensitivity of the oxygen *K*-edge to fingerprint the ultrafast population transfer to the $S_1(n\pi^*)$ state through the H-transfer intersection, the concomitant dynamics along the bond-length alternation coordinate and the subsequent re-population of the ground state. Given the coming advances in X-ray light sources, our study proposes an experimental route to disentangle photodecay pathways in MA.

References

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