

ULTRAFAST DYNAMICS OF TWO- AND THREE-BODY DISSOCIATION CAPTURED BY CORE-TO-VALENCE TRANSIENT ABSORPTION SPECTROSCOPY

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Molecular photodissociation is central to numerous photochemical processes relevant to atmospheric chemistry and photocatalysis. As platforms to understand the ultrafast excited state dynamics underlying complex molecular photodissociation mechanisms, we studied the ultraviolet photodissociation of two gas-phase molecules: acetyl iodide^a, which is a photolytic precursor for the acetyl radical, and iron pentacarbonyl^b, which is a model photocatalyst system. Using ultrafast extreme ultraviolet transient absorption spectroscopy, we followed the photodissociation dynamics of these molecules via core-to-valence transitions of their respective heavy atom constituents (I and Fe), giving access to atom-specific signatures of excited electronic states.

In acetyl iodide, we observe transient features with sub-100 fs lifetimes associated with the excited state wavepacket evolution prior to dissociation. These features then evolve to yield spectral signatures corresponding to the dissociation of the C-I bond. In iron pentacarbonyl, we observe transient features evolving on 100 fs to few-picosecond timescales due to excited state loss of carbonyl groups. We combine experimental findings with quantum chemical calculations to gain insight into the photodissociation dynamics.

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