

Abstract Submitted  
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**Probing the UV Photodissociation Dynamics of Bromoform with Femtosecond Inner-Shell Transient Absorption Spectroscopy**<sup>1</sup> B.W. TOULSON, M. BORGWARDT, H. WANG, F. LACKNER, A.S. CHATTERLEY, Lawrence Berkeley National Laboratory, D.M. NEUMARK, S.R. LEONE, UC Berkeley and Lawrence Berkeley National Laboratory, D. PRENDERGAST, O. GESSNER, Lawrence Berkeley National Laboratory — UV pump – XUV probe femtosecond transient absorption spectroscopy has been used to study the photodissociation dynamics of bromoform (CHBr<sub>3</sub>). Element-specific core-to-valence transitions provide an atomic scale perspective, sensitive to changes in the local valence electronic structure, with ultrafast time resolution. Complementary excited state molecular dynamics (MD) calculations with surface hopping explore the nuclear dynamics from which XUV spectra are calculated using time-dependent density functional theory. The XUV spectra track how the singly occupied molecular orbitals (SOMO) of transient electronic states develop throughout the C–Br bond fission, eventually forming radical Br and CHBr<sub>2</sub> products. The combination of ultrafast transient inner-shell spectroscopy and *ab initio* calculations provides detailed insight into the dynamics, indicating that a continuous change of electronic orbital characters and atomic arrangements occurs during the photochemical reaction. While a proposed sub-100 fs roaming-like isomerization pathway cannot be reproduced, the MD simulations hint that transient isomers may form on multi-100 fs timescales, albeit with a much smaller likelihood than direct CHBr<sub>2</sub> – Br scission.

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B.W. Toulson  
Lawrence Berkeley National Laboratory

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