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14. ABSTRACT

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# RPPR Final Report
as of 06-Jun-2022

Agency Code: 21XD

Proposal Number: 74811CH **Agreement Number: W911NF-20-1-0127**

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**Report Date:** 19-Dec-2021 Date Received: 16-May-2022
**Final Report** for Period Beginning 20-May-2020 and Ending 19-Sep-2021
**Title:** Tracking Hole Migration Dynamics with X-Ray Attosecond Transient Absorption
**Begin Performance Period:** 20-May-2020 **End Performance Period:** 19-Sep-2021
**Report Term:** 0-Other
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**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 1 **STEM Participants:** 2

**Major Goals:** The major goal of this project was to use attosecond transient absorption to investigate the dynamics of photoexcited molecules with unprecedented temporal resolution. In these experiments, a molecule is excited by a few femtosecond laser pulse, and the resulting dynamics are probed by transient absorption of a broadband attosecond pulse that has sufficient energy to excite core-to-valence transitions on selected atoms. By their nature, these transitions are highly element-specific, enabling one to probe how the electronic structure around a particular atom in a molecule evolves subsequent to photoexcitation. Experiments carried out in the energy range of 40-75 eV probe core-to-valence transitions on halogen atoms, while a different experimental configuration generates higher energy photons ranging from 150-350 eV, enabling excitation of these transitions on sulfur and carbon atoms.

**Accomplishments:** Two types of experiments were carried out. In the lower attosecond photon energy range (40-75 eV), the dynamics of photoexcited alkyl iodides were investigated. Here, the molecule is excited to a repulsive state with a 15-20 fs ultraviolet pump pulse centered at 270 nm, and the attosecond probe pulse excites 4d-valence transitions in the dissociating molecule. Alkyl iodides are known to undergo dissociation through a conical intersection (CI) en route to alkyl + I products, and the branching between ground state I atoms and spin-orbit excited I* atoms is determined by the dynamics associated with passage through this CI. In our experiment, the temporal resolution was high enough to observe wave-packet bifurcation as the wavefunction for photoexcited molecule, created on a single potential energy surface, splits into two during passage through the CI. This novel observation is the first of its type and provides fundamental insights into the non-adiabatic dynamics of these benchmark molecules.
The second set of experiments was performed on a different laser system that outputs attosecond pulses in the 150-350 eV range, enabling us to probe core-to-valence transitions on the sulfur and carbon atoms in photoexcited SF6 and CO2. Here, a few fs near-infrared pulse excites vibrational coherences in the target molecule via impulsive stimulated Raman scattering (ISRS). These coherences manifest themselves in attosecond transient absorption via oscillations in the core-to-valence transitions on the S and C atoms. By Fourier-transformation of these time-dependent signals, one recovers the vibrational frequencies of the target molecules.

**Training Opportunities:** This project provided training to two Ph.D. students in the Berkeley Chemistry department.

**Results Dissemination:** Two papers were published:
"Conical intersection and coherent vibrational dynamics in alkyl iodides captured by attosecond transient absorption spectroscopy" K. F. Chang, H. Wang, S. M. Poullain, J. Gonzalez-Vasque L. Banares, D. Prendergast, D. M. Neumark, S. R. Leone J. Chem. Phys 156, 114304 (2022).

"Mapping wave packet bifurcation at a conical intersection in CH3I by attosecond XUV transient absorption spectroscopy" K. F. Chang, H. Wang, D. Prendergast, D. M. Neumark, S. R. Leone J. Chem. Phys. 154, 234201 (2021).

Manuscripts describing the work on SF6 and CO2 are currently in preparation.

**Honors and Awards:** Nothing to Report

**Protocol Activity Status:**

**Technology Transfer:** Nothing to Report

**PARTICIPANTS:**

**Participant Type:** PD/PI
**Participant:** Daniel Neumark
**Person Months Worked:** 1.00 **Funding Support:**
Project Contribution:
National Academy Member: Y

**Participant Type:** Graduate Student (research assistant)
**Participant:** Kristina Chang
**Person Months Worked:** 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Andrew Ross
**Person Months Worked:** 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Partners**

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I certify that the information in the report is complete and accurate:
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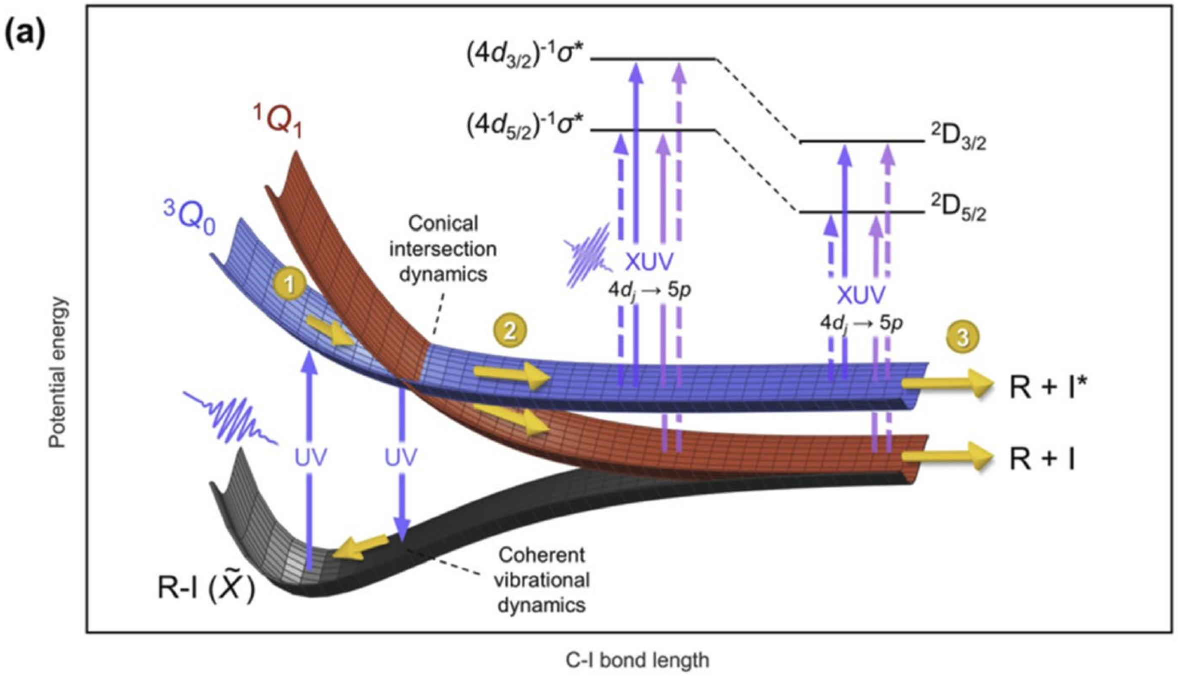

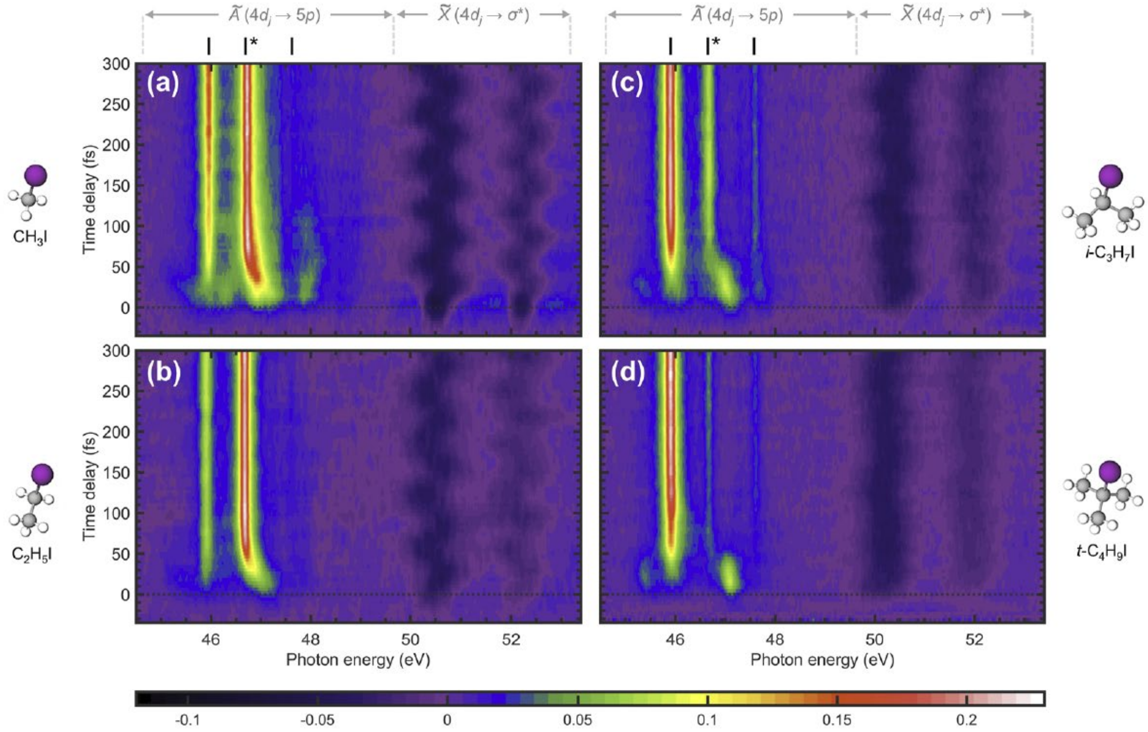

These figures are taken from "Conical intersection and coherent vibrational dynamics in alkyl iodides captured by attosecond transient absorption spectroscopy" K. F. Chang, H. Wang, S. M. Poullain, J. Gonzalez-Vasque L. Banares, D. Prendergast, D. M. Neumark, S. R. Leone *J. Chem. Phys* **156**, 114304 (2022). In these experiments, the dynamics of photoexcited alkyl iodides were investigated. Here, the molecule is excited to a repulsive state with a 15-20 fs ultraviolet pump pulse centered at 270 nm, and the attosecond probe pulse excites 4d-valence transitions in the dissociating molecule (upper panel).

Alkyl iodides are known to undergo dissociation through a conical intersection (CI) en route to alkyl + I products, and the branching between ground state I atoms and spin-orbit excited I* atoms is determined by the dynamics associated with passage through this CI. In our experiment, the temporal resolution was high enough to observe wave-packet bifurcation as the wavefunction for photoexcited molecule, created on a single potential energy surface, splits into two during passage through the CI (lower panel). This novel observation is the first of its type and provides fundamental insights into the non-adiabatic dynamics of these benchmark molecules.