

Photo-induced dynamics in bromoform molecules studied by femtosecond XUV transient absorption spectroscopy

Florian Lackner^{1,2,3}, Adam S. Chatterley^{1,2}, Benjamin W. Toulson¹, Daniel M. Neumark^{1,2}, Stephen R. Leone^{1,2,4}, and Oliver Gessner^{1*}

¹Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA

²Department of Chemistry, University of California, Berkeley, California, 94720, USA

³Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

⁴Department of Physics, University of California, Berkeley, California, 94720, USA

Abstract. Ultrafast dissociation dynamics in bromoform molecules initiated by UV (263 nm) excitation and by strong-field ionization are explored using femtosecond XUV transient absorption spectroscopy.

1 Introduction

The ultrafast photochemistry of bromoform (CHBr_3) is currently attracting great interest [1]. Here, we employ femtosecond transient inner-shell absorption spectroscopy to probe the photoinduced dynamics at the Br $M_{4,5}$ edge, providing site-specific insight from the viewpoint of the Br atoms.

2 Experimental

In the UV experiments, bromoform molecules are excited by 120 fs long, 263 nm “pump” pulses derived from the 3rd harmonic of a NIR fundamental (785 nm). XUV “probe” pulses are generated in a high-order harmonic generation (HHG) process, producing femtosecond XUV pulses covering a photon energy range from ≈ 50 eV to ≈ 72.5 eV [2-4]. Pump- and probe-beams intersect in a gas cell containing bromoform at a backing pressure of ≈ 7 mbar. The transmitted XUV light is spectrally dispersed by a grating and detected with an X-ray CCD camera. Scanning of the pump-probe time delay provides insight into the evolving dynamics on a femtosecond timescale. An overall instrument response function (IRF) of 130 fs (FWHM) is determined by monitoring the UV-induced ponderomotive shift of $np \leftarrow 4d^{-1}$ inner-shell to Rydberg transitions in Xe atoms. The UV-initiated dynamics are compared to strong-field ionization induced dynamics using the fundamental NIR laser with an IRF of ≈ 40 fs.

* Corresponding author: ogessner@lbl.gov

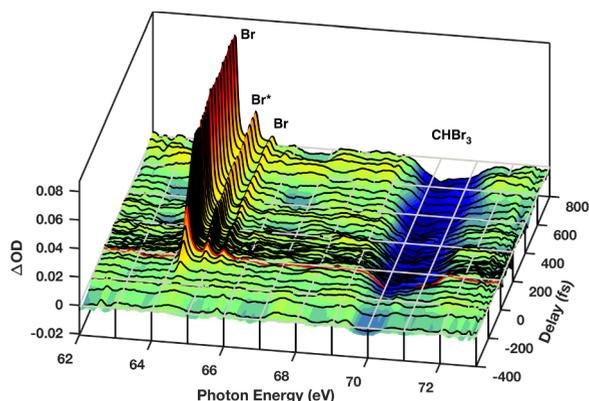


Fig. 1. Femtosecond transient inner-shell absorption spectra of bromoform (CHBr_3) molecules following excitation with 263 nm pulses at an intensity of $\sim 4 \times 10^{12} \text{ W/cm}^2$. Negative (blue) and positive (red) contributions correspond to the depletion of ground state parent molecules and the emergence of fragment Br atoms, respectively.

3 Results and Discussion

The static XUV absorption spectrum (not shown) is dominated by transitions from Br $3d_{5/2}$ and $3d_{3/2}$ core-levels into unoccupied valence orbitals, appearing as a prominent double-peak structure around 70.5 eV. The location of these features is slightly lower in bromoform than in vinyl bromide [3] or dibromoethane [4].

Figure 1 shows transient inner-shell absorption spectra, i.e., time-dependent changes of the CHBr_3 $3d^{-1}$ spectrum, after excitation with a 263 nm pulse at a pump laser intensity of $\sim 4 \times 10^{12} \text{ W/cm}^2$. The depletion of ground state bromoform molecules around 70.5 eV (blue regions, negative ΔOD) and the emergence of Br atoms (sharp peaks, positive ΔOD) are readily apparent. Based on ref. [5], the atomic Br peaks are assigned to core to valence transitions in ground state Br (${}^2D_{3/2} \leftarrow {}^2P_{3/2}$ (64.4 eV), ${}^2D_{5/2} \leftarrow {}^2P_{3/2}$ (65.4 eV)) and excited state Br* (${}^2D_{3/2} \leftarrow {}^2P_{1/2}$ (65.0 eV)) products, as indicated.

The spectral signature of neutral molecular fragments is superimposed on the parent molecule depletion signal (Fig. 2a). The two spectral contributions are decomposed by determining the difference between the measured depletion signal (blue) and an inverted copy of the static parent molecule spectrum (green), scaled to the same absolute minimum. The difference spectrum (red) is dominated by two features near ~ 71 eV and is tentatively assigned to CHBr_2 fragments based on the argument that one UV photon is sufficient to access the $\text{CHBr}_2 + \text{Br}$ asymptote but two photons are required for the production of $\text{CHBr} + 2 \text{ Br}$ [6]. A significant $\text{CHBr} + \text{Br}_2$ product channel contribution can be excluded due to the absence of Br_2 in the spectra, which would exhibit a strong absorption feature around 68.8 eV [7].

Fig. 2b shows the temporal evolution of the parent molecule depletion (black) and the emergence of Br (blue) and Br* (red) fragments. All dynamics proceed on sub-100 fs timescales, faster than the IRF. However, while a molecular fragment has been identified in the long-time delay spectrum, the present signal-to-noise ratio does not allow conclusions about transient molecular features that may be present only close to $t = 0$.

At higher UV pump intensities ($\sim 1 \times 10^{13}$ W/cm²), the instantaneous rise of a broad feature at 66.5 eV is observed (not shown). This feature is only visible near zero pump-probe delay and evolves into sharp lines for longer time delays, corresponding to the formation of Br⁺ fragments. The UV experiments are complemented by measurements on strong-field ionized bromoform, which also leads to the formation of Br, Br* and Br⁺. Interestingly, however, atomic fragments form within ~ 170 fs after strong-field ionization, significantly slower than after UV excitation.

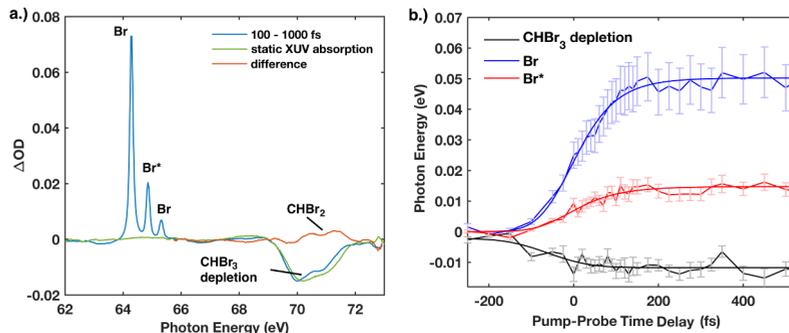


Fig. 2. UV excitation of bromoform at pump intensities of $\sim 4 \times 10^{12}$ W/cm²: a) Long-time delay spectrum (blue, average for $\Delta t = 100$ fs ... 1000 fs) and inverted static XUV absorption spectrum (green), scaled to match the depletion feature. The difference between the two spectra reveals the formation of a molecular fragment, which is attributed to CHBr₂. b) Temporal evolution of the emergence of Br (blue) and Br* (red) fragments as well as the depletion of ground state bromoform molecules (black).

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division, through Contract No. DE-AC02-05CH11231. F.L. would like to acknowledge support by the Austrian Science Fund (Grant No. J 3580-N20).

References

1. A.S. Mereshchenko, E.V. Butaeva, V.A. Borin, A. Eyzips and A.N. Tarnovsky, *Nat. Chem.*, **7**, 562 (2015).
2. F. Lackner, A.S. Chatterley, C.D. Pemmaraju, K.D. Closser, D. Prendergast, D.M. Neumark, S.R. Leone and O. Gessner, *J. Chem. Phys.*, **145**, 234313 (2016).
3. M.-F. Lin, D.M. Neumark, O. Gessner and S.R. Leone, *J. Chem. Phys.* **140**, 064311 (2014).
4. A.S. Chatterley, F. Lackner, D.M. Neumark, S.R. Leone and O. Gessner, *Phys. Chem. Chem. Phys.*, **18**, 14644-14653 (2016).
5. A. Cummings and G. O'Sullivan, *Phys. Rev. A.*, **54**, 323 (1996).
6. S.K. Pal, A.S. Mereshchenko, E.V. Butaeva, P.Z. El-Khoury and A.N. Tarnovsky, *J. Chem. Phys.*, **138**, 124501 (2013).
7. E.R. Hosler and S.R. Leone, *Phys. Rev. A* **88**, 023420 (2013).