Ultrafast Molecular Dynamics Probed Using Strong Field Ionization

Wen Li, Vandana Sharma, Craig Hogle, Agnieszka Jaron-Becker, Andreas Becker, Henry Kapteyn and Margaret Murnane

JILA and Department of Physics, University of Colorado, Boulder, CO, 80309, USA

Synopsis: We report preliminary measurements using strong field ionization to monitor the photodissociation of bromine molecules. The time dependent kinetic energy release (KER) of bromine cations (Br^+) was used to identify the molecular cation states (Br_2^+),which contribute to the production of Br^+. We observe a strong angular dependence of the Br^+ yield, representing the shape of the ionizing molecular orbital. The time evolution of the angular distribution of Br^+ was also obtained. This is the first experimental demonstration of using strong field ionization to monitor orbital rearrangement during a chemical reaction.

Electronic dynamics play a central role in chemical reactions. It is very desirable for a detection technique to have the capability of probing ultrafast electronic motion. Time resolved photoelectron spectroscopy (TRPES) [1] can provide some insights. However, the most direct information - such as mapping electron configurational changes in real time - remains elusive. Recently, strong field ionization has been demonstrated as a probe of the static electron density distribution of the HOMO orbital[2][3]. Here we report preliminary results that use strong field ionization as a probe to study electron rearrangement during the photodissociation of bromine.

The experiment was carried out using a cold target recoil ion momentum spectroscopy (COLTRIMS) apparatus. A neat bromine molecular beam enters the vacuum chamber through supersonic expansion. The photodissociation is initiated by 400 nm ultrafast laser pulses produced by second harmonic generation of the fundamental laser output. Absorption of one 400 nm photon excites the bromine from the ground state to the C ($^1\Pi_u$) dissociative state. An intense, time-delayed, 800 nm laser beam is used to ionize the dissociating bromine molecules to produce Br^+. The momentum distributions of Br^+ at different pump-probe delays are then recorded. Figure 1 shows the kinetic energy release of Br^+. By comparing these data with theoretical calculations, we conclude that the slow Br^+ at early time delay is generated from states arising from removing an electron from a π_u orbital, while the fast Br^+ at later time delays are from ionization of an σ_g orbital.

The yield of fast Br^+ reaches a maximum when the angle between the Br-Br internuclear axis and the probe laser polarization is zero, and monotonically decreases when the angle increases. This is in good agreement with theoretical predictions if a σ_g orbital is ionized. The time evolution shows a narrowing angular dependence of Br^+ yield, which also matches preliminary theoretical calculations.

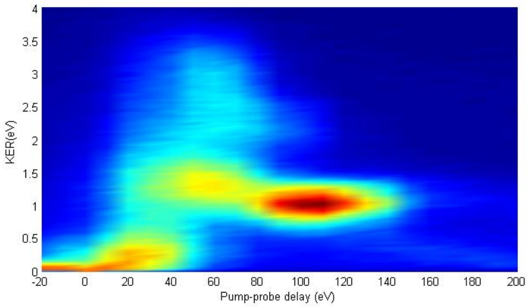

Fig. 1. Time dependent KER of Br^+.

It is also interesting to note that the Br^+ yield peaks around 100 fs (Fig. 1). At this time delay, the Br-Br internuclear distance reaches about 4.2 Angstroms. The origin of this enhancement of the ionization is unclear. Charge resonance enhanced ionization (CREI) is one possible explanation.

In summary, we demonstrate that strong field ionization can be used as a probe of molecular dynamics, in particular of electron rearrangement during a chemical reaction.

References

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E-mail: wli@jilau1.colorado.edu