Ultrafast photodissociation of Br$_2$: Laser-generated high-harmonic soft x-ray probing of the transient photoelectron spectra and ionization cross sections

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The ultrafast dissociation of gas-phase Br$_2$ is probed via a 400 nm pump soft-x-ray probe scheme at five different high-order harmonic wavelengths (13th, 15th, 17th, 19th, and 21st of an 800 nm Ti:sapphire laser). A series of time-resolved ultrafast photoelectron spectra reveals prompt two-photon ionization features, which allow in situ measurement of the cross correlation between the pump and probe pulses. Transient features are attributed to ionization of the dissociative excited state wave packet, and new spectral peaks are associated with the formation of atomic Br.

Deconvolution of time-trace plots of the atomic signals with the cross-correlation pulse durations reveal similar dissociation times (~40 fs) at two probe wavelengths (47 and 42 nm). Analysis of the transient wave packet photoelectron signal suggests an ionization process that occurs during dissociation, with a broad electron kinetic energy distribution at an extended Br–Br bond length (R > 3 Å). At long delay times (>500 fs), an enhancement of the ionization cross section of the Br atom compared to the Br$_2$ molecule is observed with each of the probe wavelengths, the ratio increasing from a factor of 21±1 to 56±5 for probe wavelengths of 61.5 to 38 nm, respectively. The intensity of the transient wave packet signal on the dissociative state remains nearly constant between the 17th and 19th harmonic probes, indicating that the ionization cross section of the dissociative state has an entirely different wavelength dependence than the Br atom. The transient wave packet ionization signal is qualitatively 10%–20% of the simultaneous two-photon (400 nm + soft x-ray) ionization signal. The results are discussed in terms of the transient dynamics of dissociative state photoelectron spectroscopy, the correlation between molecular and atomic ionization probabilities, and above threshold ionization probabilities. © 2002 American Institute of Physics. [DOI: 10.1063/1.1504084]

I. INTRODUCTION

Ultrafast pump–probe spectroscopy has proven to be a successful tool for understanding fundamental physical processes that occur on picosecond and subpicosecond time scales. One important application of ultrafast spectroscopy is investigating the nature of the chemical bond by probing the evolving electronic structure of a molecule during a chemical reaction or molecular dissociation. Ultrafast soft-x-ray pulses provide a unique opportunity to probe this electronic structure via photoelectron spectroscopy. The photoelectron spectrum at a particular time delay after a reaction is initiated contains information about the electronic structure of the reactants and products. Several questions arise: How does the electronic structure progress in time? Is the transition between reactants and products smooth or instantaneous? What is the nature of ionization from the excited state? Visible-pump soft-x-ray probe experiments have the potential to investigate these questions and the nature of bonding in chemical reactions. While several similar experiments have been reported that explore condensed phase dynamics, here we describe a unique gas phase study of a fundamental diatomic molecule system.

Utilizing a novel 400-nm-pump soft-x-ray probe setup coupled with a photoelectron spectrometer, we examine in detail the photodissociation of Br$_2$ on an ultrafast time scale. Bromine was chosen as the molecule for study due to its straightforward static photoelectron spectrum and its relatively strong absorption cross section (5 x 10$^{-19}$ cm$^2$) at the pump wavelength of 400 nm, which excites a single dissociative state. These experiments aim to understand how the bonding in Br$_2$ evolves after excitation to the C $^1Π_u$ dissociative state, the appearance of Br atoms, and the issues surrounding ionization from excited states. The results presented here demonstrate that a number of complex aspects exist even in a simple system, including simultaneous two-photon ionization (called above threshold ionization in atoms where there is not a dissociative electronic state involved), cross-correlation features vs transient signals, the onset of atomic photoelectron signals, multiple final ion states, and issues of atomic and transient state ionization cross sections.

Building on preliminary results, here we analyze in
The Br$_2$ molecule is excited to the dissociative state with the 400-nm pulse, the soft-x-ray pulse ($\lambda$$_{\text{probe}}$). The excited molecule and/or products at a specified time delay ($\Delta t$). Ejected photoelectrons from the soft-x-ray ionization are collected in a time-of-flight magnetic-bottle electron energy analyzer. The photoelectron spectrum gives an instantaneous picture of the ionization region via the background unexcited Br$_2$; (2) simultaneous two-photon ionization of Br$_2$ (400 nm + $\lambda$$_{\text{probe}}$); (3) ionization of the Br$_2^*$ wave packet at an extended bond length before dissociation; and (4) ionization of Br atom products. Analysis of the time dependence of the last three types of signals yields information on the dynamics of electron rearrangement during dissociation on a femtosecond time scale.

A study of the ionization cross sections of the Br atom compared to the Br$_2$ molecule is presented using several probe wavelengths, from the 13th to the 21st harmonics of 800 nm. An enhancement of the Br atom ionization cross section produces a corresponding enhancement of the observed photoelectron signal of the atoms, which in turn allows for more facile detection of the atomic pump–probe signal above the background single-photon ionization signal of the molecule. When a population is created in the excited state with the 400-nm pulse pump, a corresponding fraction of dissociated molecules can be calculated. Using the number of molecules pumped into the excited state (calculated from the molecular absorption cross section and the number of photons in the pump beam) and the observed photoelectron signals, it is possible to calculate a relative cross section enhancement, $\sigma$$_{Bl}$/$\sigma$$_{Br}$. The cross-section for the wave packet on the molecular dissociative state relative to the simultaneous two-photon ionization process is also estimated. The variations in the cross sections at the soft-x-ray wavelengths will require further theoretical interpretation to understand future pump–probe studies with soft-x-rays.

II. EXPERIMENT

The experimental apparatus has been described in detail elsewhere, but a brief description is given here. Pulses from a commercial 70 fs, 1000 Hz, 800 nm Ti:sapphire laser are split into probe and pump beams, respectively, with an 80/20 beamsplitter (Fig. 1). The transmitted beam (~1.7 mJ) is sent through a stepper-motor controlled delay stage and focused into a pulsed gas jet of argon, where high-order harmonics (odd harmonics from the 9th to the 23rd) are created.

The soft-x-ray beam, comprised of all the harmonics and residual 800 nm light, is incident on a concave spherical grating where the desired harmonic is selected. A temporal stretching effect occurs by using a grazing incidence grating; therefore, a second grating is incorporated to compensate and temporally recompress the soft-x-ray pump pulse. This second toroidal grating is also an effective focusing optic, and the soft-x-ray beam is focused to a spot diameter of ~150 $\mu$m. While very short soft-x-ray pulses are expected from the harmonic generation process, the use of two gratings introduces additional linear chirp to the pulse. Pulses of the harmonics generated in argon contain on the order of ~3 x 10$^6$ photons/pulse, with harmonic-dependent temporal widths in the interaction region of 950 fs (13th), 600 fs (15th), 250 fs (17th), 190 fs (19th), and 250 fs (21st). The pump beam (0.4 mJ), which is reflected by the beam splitter, is frequency doubled in a 0.1-mm-thick BBO crystal creating 140 $\mu$J, 80 fs, 400 nm pulses. A mirror inside the vacuum chamber directs the pump beam into the interaction region of the photoelectron spectrometer. The temporal and spatial overlap of the UV and soft-x-ray beams is optimized using above threshold ionization photoelectron signals in Xe.

The gaseous sample (Br$_2$) is introduced into the interaction region via an effusive flow nozzle with sample densities of 1.6 x 10$^{12}$ molecules/cm$^3$. As the pump and probe beams are incident on the bromine molecules, photoelectrons are ejected and energy analyzed in the differentially pumped magnetic-bottle time-of-flight spectrometer. Photoelectrons are collected with a microchannel plate detector, and the signal is amplified and recorded with a multichannel scalar linked to a computer. Pump–probe spectra are taken in time steps of either 33 or 66 fs by moving the delay stage in steps of 5 or 10 $\mu$m, respectively (effectively increasing the optical path length by 10 or 20 $\mu$m). A typical photoelectron spectrum is a coaddition of electrons collected during 100 000
laser pulses. Two methods are used to subtract pump-on photoelectron spectra from pump-off spectra. The first is to take a series of photoelectron spectra with the soft-x-ray pulse arriving at the sample $\geq 500$ fs before the 400 nm pump pulse (negative time delay). The average of these spectra is then subtracted from the pump–probe spectra in the overlap region and at positive time delays ($-200$ to $+1000$ fs). The second method is to use an optical chopper that reduces the pump beam to 500 Hz. The soft-x-ray pulse remains at 1000 Hz, and even and odd pulses are then recorded as two sets of photoelectron spectra, pump-on and pump-off, by two separate multichannel scalar collectors. The pump-off spectrum is subtracted from the pump-on spectrum. For this experiment, the former method was used, as better signal to noise was achieved in the subtraction. Subtracted and unsubtracted spectra are typically smoothed by a factor of 5.

III. RESULTS AND DISCUSSION

A. Pump–probe photoelectron spectra in Br$_2$

By collecting a series of photoelectron spectra at varying pump–probe time delays, several ionization processes are directly observed. After careful analysis of the time-correlated photoelectron signals, one can gain new insight into the electron distribution within the molecule during the ultrafast dissociation of Br$_2$. Figure 2 gives a simplified potential energy curve diagram of the Br$_2$/Br$_2^+$ system, taken from Refs. 22 and 23. In this diagram is illustrated the possible ionization processes in a time-evolving system, including (1) the background signal from ground-state ionization by the high-energy harmonic probe; (2) the simultaneous two-photon ionization cross-correlation signals where the pump and probe beams overlap at zero pump–probe delay; (3) the ionization of the excited state wave packet as it evolves along the dissociative curve, but before dissociation is complete; and (4) the ionization of the final Br atom products. The diagram shows only the X and C electronic states of neutral Br$_2$ and the X and A states of Br$_2^+$ for simplicity, since these are the important electronic states involved in the photodissociation and ionization processes in the pump–probe experiment presented here.

Figure 3 illustrates a sampling of the observed photoelectron spectra in Br$_2$ using a 400 nm pump pulse and a 17th harmonic (47 nm, 190 fs) probe pulse. The region from 7.0 to 12.5 eV binding energy is highlighted, which contains all the relevant photoelectron features. The spectra correspond to pump–probe delays ranging from $-300$ fs (bottom), where the 17th harmonic pulse arrives in the interaction region before the 400 nm pulse, to $+300$ fs (top) where the 400 nm pulse arrives first. The five time-correlated features observed are marked with vertical dashed lines in Fig.
3. The first feature centered at 7.4 eV binding energy reaches a maximum at zero time delay ($t=0$) and is attributed to process (2) in Fig. 2, referred to as “simultaneous two-photon ionization,” where the temporal overlap of the 17th harmonic probe and UV pump pulses creates a photoelectron feature due to the two-photon ionization of Br$_2$. It appears at a binding energy that is 3.1 eV lower than the one-photon ionization feature at 10.5 eV binding energy from the $X \rightarrow X^+$ transition. The sequence of photon absorption and ionization for such a two-photon process could occur in one of two ways. Either the 400 nm pulse promotes a wave packet resonantly from the neutral ground state to the excited dissociative state followed by instantaneous ionization by the 17th harmonic [as shown in process (2a) of Fig. 2], or it is the result of a purely above threshold ionization process (ATI) where the 17th harmonic ionizes Br$_2$ and the 400 nm adds to the ionization energy at $t=0$ [(2b) of Fig. 2]. On the one hand, it is believed that the excited state wave packet is directly observed at a later positive time delay (discussed below). On the other hand, ATI processes involving the harmonics and 400 nm pulse are readily observed in other gases that do not have dissociative states (such as Xe). Therefore, we believe the observed signal is likely a combination of the two processes. The feature at $-9.6$ eV binding energy (3.1 eV shifted from the 12.7 eV one-photon ionization $X \rightarrow A^+$ peak) is attributed to a similar two-photon ionization, except that the Br$_2^+$ ion is left in the excited A state. Both of these two-photon ionization signals provide an internal cross correlation between the soft-x-ray probe and 400 nm pump pulses during the dissociation experiment. Additionally, a third cross-correlation feature is expected, leaving the ion in the excited B state. However, this feature should appear at a binding energy of 11.4 eV, a region already congested with both background and atomic signals.

The second type of photoelectron feature at 8.4 eV does not correspond to a 3.1 eV shift from any of the one-photon ionization features, and therefore it cannot be a cross-correlation signal as described above. Inspection of processes (2) and (3) of Fig. 2 reveals that the photoelectron energy in process (3), which results from ionization of the excited state wave packet as it slides out on the dissociative curve, should occur at a photoelectron energy between the two cross-correlation photoelectron peaks in process (2). This explanation is consistent with the observed time-correlated signal in the photoelectron spectrum at 8.4 eV binding energy. The time dependence and intensity of this transient ionization signal are discussed in more detail in a later section (see Sec. III C). The last type of photoelectron signals in Fig. 3 corresponds to the known binding energies of the Br atom states (11.6, 11.95, and 12.0 eV, corresponding to the $3P_{2,1,0}$ states of Br$^+$, respectively$^{24}$). The atomic photoelectron signals appear nearly instantaneously compared to the maximum of the cross-correlation signal. This phenomenon is analyzed in detail in the following section.

B. Time traces of cross-correlation and Br atom signals

By comparing the time traces of the in situ cross-correlation signal and the atomic signals, it is possible to extract a dissociation time of the Br$_2$ molecule and compare this with predicted time scales and bond distances for dissociation on calculated potential curves. Time traces are created by plotting the total electron counts in the cross-correlation peak ($X \rightarrow X^+$ peak only) and the atomic peaks vs pump–probe delay (see Fig. 4). Figure 4(a) represents data points taken from Fig. 3 (and additional photoelectron spectra not shown) with the 17th harmonic as the probe beam. The cross-correlation trace between pump and probe pulses is fit by a Gaussian curve according to the following equation:

$$ S(t) = S_0 + A \times \exp \left[ -4 \ln 2 \left( \frac{(t-t_0)}{\sigma_{\text{fwhm}}} \right)^2 \right], \quad (1) $$

where $S_0$ is an offset background signal, $A$ is the peak height (normalized to 1.0), $t_0$ is the time value at the peak of the pulse, and $\sigma_{\text{fwhm}}$ is the full width at half maximum of the cross correlation. The fit of the cross-correlation data in Fig. 4(a) by Eq. (1) yields a $\sigma_{\text{fwhm}} = 340 \pm 16$ fs and peak time $t_0 = 0 \pm 6$ fs.
The total atomic signal is fit with a smoothed step function given by the following equation:

\[
S(t) = A \times \frac{1}{2} \text{erf}\left(\frac{(t - \tau_{\text{step}})2 \sqrt{\ln 2}}{\sigma_{\text{fwhm}}}\right) + \frac{1}{2} + S_0, \tag{2}
\]

where \(S(t)\) is the total signal, \(\tau_{\text{step}}\) is the average time delay between a hypothetical instantaneous photon absorption and product atom formation, and \(\sigma_{\text{fwhm}}\) is the full width at half maximum of the above-mentioned Gaussian. In addition, the fitting parameters \(S_0\) and \(A\), which are the offset background signal and peak height, respectively, are added to fit the raw data. The data are then normalized to ensure that the step function amplitude is confined to values from 0 to 1. The fit incorrectly estimates the background and the height, the result remains valid in the region 2.5 Å ≤ \(R\) ≤ 3.5 Å. The experimental result of 40 fs implies a bond distance of \(\sim 3\) Å, while a bond distance of 2\(R_e\) occurs at a time of 105 fs.

\[
U(R) = U_{\text{limit}} + \frac{1.594 \times 10^7}{R^{9.384}} \text{cm}^{-1}. \tag{3}
\]

The total energy of the system is calculated according to the equation: \(E_T = \text{K.E.} + \text{P.E.} + \text{kinetic} + \text{potential} + \text{energy.}\) The total energy, \(E_T\), put into the system is simply the energy of a 400 nm photon, \(\text{K.E.} = \frac{1}{2} \mu (\text{d}R/\text{dt})^2\), and an equation estimating the shape of the dissociative potential energy curve (P.E.) is given below.

\[
t_d = \left(\frac{2}{\mu} (E_T - U(R))^{-1}\right) \text{ d}R. \tag{4}
\]

Numerical integration of Eq. (4) results in a curve that relates dissociation time and internuclear distance of the \(\text{Br}_2\) \(C\) excited state [see Fig. 5(b)].

According to the resulting curve from the integration of Eq. (4), in 40 fs the Br–Br separation will have reached \(\sim 3\) Å from an initial ground-state equilibrium bond distance of \(R_e = 2.23\) Å.\(^{22}\) While isolated atomic behavior at such a bond distance is possible, one might also expect contributions from the dissociating wave packet over several regions of the dissociative curve, which would result in a broad peak in the atomic region at early time delays. Then, at later time delays, the atomic peak should become narrower as the dissociation is nearly complete. The designation \(2R_e\) in Fig. 5 represents a bond distance where dissociation to two Br atoms is likely complete, occurring at a delay time of \(\sim 105\) fs. Naturally,
the temporal width of the probe pulse introduces some limitation in being able to observe broadened features. In addition, a step function model for production of the atomic features is not the most accurate description of the dissociation. While the step function picture is useful in extracting an upper limit on the dissociation time, information about energy redistribution during the dissociation process is contained in the transient photoelectron features discussed in the following sections.

C. Ionization of the excited state wave packet

While analysis of the pulse cross-correlation vs atomic signal rise yields important information, to study the dynamic photodissociation process a signature from the Br$_2$ molecule in a state between the molecule and atom is desired. The analysis of such a photoelectron signal, resulting from ionization of the excited state wave packet before dissociation is complete, is analyzed in detail here. An expanded photoelectron spectrum highlighting the transient signal of interest as well as the cross-correlation features is shown in comparison to a background spectrum (gray line) in Fig. 6. A broad photoelectron feature between the cross-correlation signals is clearly observed. The time-dependent intensity of this signal is a clue to the electron rearrangement during the ultrafast dissociation process. In Fig. 7, four time traces are extracted from the same pump–probe photoelectron spectra reported here, using both the 17th (a) and 19th (b) harmonics as a probe. Features at different electron kinetic energies are all collected here onto similar pump–probe time traces. Figure 7 compares the cross-correlation signal leaving the Br$_2^+$ ion in the X state (corresponding to the area under the peak from 6.5 to 8 eV binding energy in Fig. 6), the cross-correlation signal leaving the ion in the A state (9–9.5 eV), the transient signal (8–9 eV), and a random sampling of background signal from 5–6 eV binding energy. The transient signal clearly rises above the random noise trace in both the 17th and 19th harmonic data, and it has a similar Gaussian shape and width to the cross-correlation traces. This is consistent with what would be expected if the excited state wave packet were ionized after moving just slightly out on the dissociative curve. As energy is deposited into kinetic energy of the atoms, less energy is available to the electrons.

As mentioned earlier, there are two competing two-photon processes: (1) ATI, where the harmonic ionizes Br$_2$ followed by adding one 400 nm photon above the ionization threshold, and (2) the promotion of the excited state wave packet on the dissociative state by the 400 nm pulse followed by ionization with the harmonic. These are indistinguishable at t=0, because the photoelectron possesses the same energy. If the excited wave packet moves out on the dissociative curve and is then ionized [Fig. 2, panel (3)], however, the photoelectron peak will appear at a lower photoelectron energy. This can occur since the wave packet quickly moves down the steeply sloped section of the dissociative curve and then moves more slowly in comparison when reaching the flatter section. The position of the transient photoelectron peak (Fig. 6) indicates that the wave packet is ionized at an energy of ~16 500 cm$^{-1}$ on the $^1II_u$ curve. Looking at the shape of the curve in Fig. 5(a), it is reasonable to assume that
the wave packet quickly falls down the steep slope from 24 000 to 16 500 cm$^{-1}$, and is then ionized from the flatter part of the curve, in this case at $R=3$ Å.

Scans averaged over a longer time period (in order to increase signal to noise) were also taken of this transient signal from time delays of $-33$ to $+165$ fs with the 17th harmonic as a probe (better signal to noise). The relevant part of the photoelectron spectrum for these time delays is shown in Fig. 8(a), as well as time traces for the cross correlations and transient state Fig. 8(b). These photoelectron spectra are plotted with photoelectron energy on the x axis instead of binding energy, as in Fig. 6. Again, it is clear that the transient signal (shaded region from 4.9 to 5.5 eV) rises above the random noise signal and has a structure similar to the cross-correlation features. From these time traces, as well as from Fig. 7, the peak of the transient signal is slightly delayed in time from the peak of the cross-correlation traces. This is also consistent with the wave packet being ionized after it has moved out on the dissociative curve with a small time delay. However, this observed delay between the peak of the cross correlation and the peak of the transient signal time trace is very small (10–20 fs) and it is difficult to be certain of such a small time delay with errors of $\sim 10$ fs in the deconvolutions of $t=0$ and cross-correlation FWHM measurements.

Not only does the appearance of the transient signal appear to be slightly delayed, it also seems to change shape on very short time scales ($\sim 30$ fs), as is seen in Fig. 8(a). However, it should not be possible to observe fast oscillations due to constraints of the experimental time resolution ($\approx 200$ fs), and such variations must be due to random noise fluctuations. If the wave packet is ionized from the flatter part of the dissociative curve, as discussed below, one would expect a decrease in photoelectron energy with increasing delay time, due to the shape of the Br$_2^+$ X curve. Experiments with even shorter time resolution probe pulses will be necessary to elucidate whether such shifts do occur.

D. Ionization cross sections of atoms and transient states

Another observation from the series of pump–probe photoelectron spectra considered here is the obvious difference in the ionization cross section between the bromine molecule and the atom at the 47 nm probe wavelength, first reported in Ref. 13. The enhancement of the atomic signal (as well as two-photon and transient signals) compared to the decrease in the molecular signal raises interesting questions about pump–probe spectroscopy with soft-x-rays. To attempt to fully understand this readily apparent enhancement in the pump–probe photoelectron spectra, the probe wavelength was varied by using several different harmonics (from the 13th to the 21st) as the probe. Photoelectron spectra from these harmonics, taken at long time delays well after the atomic peak has reached its maximum value ($\sim 500$ fs), reveal that the atomic signal increases smoothly with decreasing harmonic number, as is illustrated in Fig. 9. As the energy of the probe approaches the threshold for ionization, the cross section increases. Figure 9 also demonstrates that there is still an enhancement of the atomic signal over the neutral Br$_2$ background signal even for the highest harmonic studied (21st).

The value of this cross-section enhancement (designated as $\sigma_{Br_2}/\sigma_{Br_2^+}$, or the ratio of the ionization cross sections) can be calculated for each harmonic from the photoelectron spectra in Fig. 9 and experimental parameters as follows: From the reported absorption cross section of neutral Br$_2$ (5 $\times$ 10$^{-19}$ cm$^2$) and laser energy at 400 nm, an estimated 0.02% of the molecules in the interaction region reaches the excited dissociative state, leaving the rest in the ground state. To determine the relative ionization cross section between the atomic and molecular bromine at the probe wavelength,
the counts in the atomic peaks are compared to the total counts in the A-state molecular peak. Any decrease in the molecular A-state signal due to the presence of the 400 nm pump beam is imperceptible; therefore, it is estimated as being less than the noise level of the data (0.8% of the total A-state signal). This number is used only in the estimation of the error in $\sigma_{B+}/\sigma_{Br_2}$. The atomic peak, on the other hand, increases by $\sim 5\%$ of that same A-state signal (for the 17th harmonic). The areas under the peaks in Fig. 3 are not representative of the total counts used in the calculation, because the A state appears compressed on the energy scale. The A-state signal is in turn $\sim 30\%$ of the total signal originating from the ground state of neutral Br$_2$ (constant for all harmonics studied). From these numbers, and including the stoichiometric ratio of Br$_2$ to Br, we calculate the ratio of the atomic and molecular cross section for each harmonic in Br$_2$.

The results of these calculations are given in Table I. The reason for the observed cross-sectional enhancement is unclear. It is reasonable to assume that there is not a large resonance in the atomic ionization cross section, as the enhancement varies smoothly over the range of harmonics studied. It is possible that a Cooper minimum (a minimum in the partial cross section as a function of photon energy, caused by a change in sign of the dipole matrix element) in Br$_2$ causes the molecular cross section in this range to be low. If this were true, the atomic cross section could be an order of magnitude larger than the molecular cross section, in agreement with the observed results. Calculations of the molecular and atomic cross sections in this specific energy region are needed to fully explain the observed results.

In addition, the final cross-section enhancement factors are plotted vs harmonic photon energy in Fig. 10. The values in Fig. 10 are consistent with the trend observed in Fig. 9. It also follows from Fig. 10 that the 17th harmonic probe energy does not hit a resonance in the ionization cross section for Br, but that the cross section is similarly enhanced for neighboring harmonics (although to varying degrees). Even though the atomic signal is enhanced by a factor of $\sim 20$ for the 21st harmonic, it is barely visible above the background noise.

In the energy range of 20–30 eV, the Br$_2$ ionization cross section remains constant, as is evidenced by the fact that the total counts in the static photoelectron spectrum do not change significantly from the 13th to the 21st harmonics under similar experimental conditions. Thus, the reason for the trend in Fig. 10 must lie in the atomic ionization cross sections. Experimental and calculated results for the Br ionization cross section show only a slightly increasing value from $\sim 1$ to $1.5 \times 10^{-17}$ cm$^2$ in the energy region of 20–24 eV, right below the $4s~4p^5~3P$ threshold (24.1 eV). This range includes the 13th and 15th harmonics. It could be argued that the 17th harmonic is just out of this range, but is only slightly above threshold, so that the cross section is still enhanced. The 19th and 21st harmonics, however, are far above the resonance (+6–9 eV) and thus the ionization cross section drops by a factor of 2.

An important scientific question is whether the ionization cross section of the dissociative molecular state is similarly enhanced. If not, a broad signal originating from the dissociative state of the molecule in the atomic photoionization energy region may be easily obscured. Similarly, cross-correlation features from the above threshold ionization process can mask photoelectron signals arising from transient states. In an attempt to quantify this phenomenon, the percentage of the transient signal at 8.4 eV binding energy is calculated from three different pump–probe experiments [Figs. 6(a) and (b), and 8]. In other words, the total two-photon signal is calculated by integrating under the pump–probe curve in Fig. 6, and the fraction of each type of signal is calculated (two-photon cross-correlation signals leaving the Br$_2^+$ in the X and A states, and the transient signal). The results of this analysis are given in Table II.

Interestingly, the fraction of transient signal observed does not change dramatically when going from the 17th to

<table>
<thead>
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<th>Harmonic</th>
<th>$\sigma_{B+}/\sigma_{Br_2}$</th>
<th>Error%</th>
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<tr>
<td>13</td>
<td>56.1</td>
<td>5.46</td>
</tr>
<tr>
<td>15</td>
<td>48.8</td>
<td>1.64</td>
</tr>
<tr>
<td>17</td>
<td>46.1</td>
<td>4.91</td>
</tr>
<tr>
<td>19</td>
<td>25.7</td>
<td>1.64</td>
</tr>
<tr>
<td>21</td>
<td>21.7</td>
<td>0.81</td>
</tr>
</tbody>
</table>

*Based on the error from averaging several scans with identical detector and flight tube voltage settings, as well as the pressure of Br$_2$. |

<table>
<thead>
<tr>
<th>Harmonic</th>
<th>Enhancement factor ((\sigma_{Br}/\sigma_{Br+}) total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>21.7</td>
</tr>
<tr>
<td>15</td>
<td>17.7</td>
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<td>17</td>
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<td>19</td>
<td>9.7</td>
</tr>
<tr>
<td>21</td>
<td>5.7</td>
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</table>

**TABLE II.** The percentages by total counts of the cross-correlation and transient photoelectron signals for three different data sets at two probe wavelengths.

<table>
<thead>
<tr>
<th>Scan</th>
<th>Figure</th>
<th>% X ATI(^a)</th>
<th>% A ATI(^a)</th>
<th>% X transient(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17h+400 nm</td>
<td>7(a)</td>
<td>53.9</td>
<td>33.1</td>
<td>13.0</td>
</tr>
<tr>
<td>19h+400 nm</td>
<td>7(b)</td>
<td>56.6</td>
<td>34.7</td>
<td>8.6</td>
</tr>
<tr>
<td>19h+400 nm</td>
<td>8</td>
<td>54.4</td>
<td>33.2</td>
<td>12.4</td>
</tr>
</tbody>
</table>

\(^a\)Labeled ATI, but includes ATI plus direct ionization of the wave packet at $t = 0$. |

\(^b\)The total two-photon signal in Fig. 6.
the 19th harmonic, while the atomic cross section is reduced by a factor of 2 from the 17th to the 19th. This points to the possibility that the cross-sectional enhancements might be different for transient molecular states than for the final atomic products. This type of information will be crucial when measuring the time dynamics of transient states. In a simplistic molecular orbital picture, the electron ionized from the $C_1^1\Sigma_u$ state is in the $\sigma_g$ orbital, comprised of two $p_z$ Br atomic orbitals with only $\sigma$ overlap. Ionization from this diffuse orbital could account for the relatively small two-photon signals compared to the atomic signals.

IV. CONCLUSIONS

In a simple molecule (Br$_2$), we demonstrate several challenging issues that must be understood when interpreting ionization signals from excited states and excited state photodissociation dynamics. Electron distributions from excited neutral to ion states, the complication of above threshold ionization features, the time-dependent appearance of atomic photoelectron signals, the enhancement of ionization cross sections of atomic species vs molecular species, and the shapes and cross sections of signals arising from excited transient states are all relatively unexplored phenomena. We extract an ~40 fs delay time between the peak of the cross correlation and the rise of the Br atomic signals, giving an estimate of the fast dissociation time of the Br$_2$ molecule. A photoelectron signal arising from ionization of the Br$_2$ molecule at an elongated bond length is further analyzed, and it is found to have a similar temporal structure as the cross-correlation signals. Calculation of cross-sectional ratios for both the Br atom and Br$_2^*$ transient states compared to the neutral Br$_2$ molecule reveal that an enhancement in the ionization cross section exists for these species, allowing them to be easily detected when otherwise they would be buried in background counts of the parent molecule. This study of Br$_2$ gives a first glimpse into the complex nature of electron rearrangement during a dynamic, ultrafast photodissociation process.

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