Direct Observation of Excited State Fragments Following Molecular Ionization and Dissociation in Strong Fields

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Using a new double pulse technique, we have observed for the first time that charge asymmetric dissociation in diatomic molecules leaves one of the fragments in an electronically excited state. For example, we observed the reaction $I_2 + (\text{pulse 1}) \rightarrow (I_2^{2+})^{**} \rightarrow I^{0+} + (I^{2+})^* + (\text{pulse 2}) \rightarrow I^{0+} + I^{3+}$, demonstrating that the I^{2+} fragment must have been in an excited state. More generally, just as asymmetric dissociation implies that the initial molecular ion is in an excited electronic state, the observation of asymmetric channels in the postdissociation ionization shows that the ionic fragments are themselves electronically excited.

In strong field ionization, final electronic state analysis has been largely neglected. Attention has been primarily focused on ionization rates from a particular initial state rather than the final state of the atom or molecule following ionization. Sequential atomic ionization follows well-understood ionization rates [1] and is independent of any internal structure [2]. This assumes that the initial electronic state of the atom or ion is its ground state, implying that little population is left in excited states. A variety of experiments, however, show that molecules can be left in highly excited electronic states with large branching ratios. These experiments include the observation of charge asymmetric dissociation (CAD) in N_2 [3–5], O_2 [3,6], and I_2 [7–9], vacuum ultraviolet (VUV) fluorescence from N_2 [10], and the wavelength dependence of CAD channels [3]. Here, charge asymmetric means a charge difference greater than one. Given the experimental evidence that a molecule can be left in an electronically excited state by strong field ionization, it is important to ask what the relaxation processes for these excited states are and whether they can be controlled. This excitation energy can be converted either into radiation [10], kinetic energy of the dissociation fragments [3–9], or, more significantly, into electronic excitation of the fragments. The latter, although not previously observed, could provide the basis for efficient and controlled production of excited state ions. With a new double pulse technique called correlated ion spectroscopy (CIS) we can obtain information about the state of the fragments and we have, indeed, observed that CAD can lead to fragments in singly and multiply excited electronic states.

Single laser pulse measurements using time-of-flight (TOF) spectroscopy cannot directly reveal whether or not an ion resulting from strong field ionization is in an electronically excited state. Double pulse techniques provide additional information and have been used in strong field physics to show the existence of enhanced ionization at a critical internuclear separation [11], to give experimental evidence for the molecular stabilization

hypothesis in strong fields [12], to measure the structure and dynamics of internuclear wave packets [13], and more recently to study the dissociation dynamics of D_2^+ [14]. In the following experiments we use a new double pulses technique, CIS, to determine the state of the fragments as illustrated by the following example:

$$I_2 + (\text{pulse 1}) \rightarrow (I_2^{2+})^{**} \rightarrow I^{0+} + (I^{2+})^* + (\text{pulse 2})$$
$$\rightarrow I^{0+} + I^{3+}. \qquad (1)$$
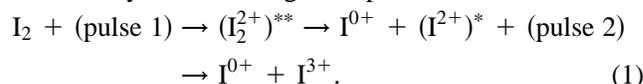
The first pulse creates an excited molecular state leading to CAD. In the second ionization step the I^{0+} acts as a probe of the absolute intensity in that the intensity must be below the threshold for ionization. The observation that $(I^{2+})^*$ does ionize shows that it must be in an excited state. Although we cannot directly detect the neutral atom, we can infer that it did not ionize based on the kinematics of the I^{3+} ion, as will be discussed, in detail, below.

CIS also allows us to solve the problem of identifying neutral dissociation channels through correlations. Until now, for diatomic molecular dissociation $I_2^{m+n} \rightarrow I^{m+} + I^{n+}$, the $m+$ and $n+$ fragments could be identified through correlations only if neither was a neutral. Furthermore, correlations are difficult to detect if there is an overlap of the $m+$ or $n+$ peak with other peaks in the TOF spectrum. These limitations can be overcome by varying the delay between the two pulses in the CIS technique. This additional degree of freedom allows us to completely determine a dissociation channel by simply measuring the kinetic energy of one fragment as a function of pulse delay.

In CIS, the first laser (pump) pulse creates some initial molecular charge state, I_2^{m+n}, which then dissociates into the fragments, $I^{m+} + I^{n+}$, hereafter labeled as (m, n). The second (probe) pulse is delayed by a time, τ, and further ionizes the fragments I^{m+} and I^{n+} to I^{m+i} and I^{n+j}, respectively. Measurements are made on the energy of the resulting double pulse channel, $(m + i, n + j)$, from just one fragment as a function of time delay. The measured energy comes from two sources: the initial dissociation

energy of the (m, n) channel and the additional energy gained when the second pulse projects the dissociated molecule onto the $(m + i, n + j)$ potential energy curve. Since the Coulomb energy gained depends on the fragment separation, the latter energy will depend on the time delay. Ultimately, this time dependence can be used to determine the charge state of the undetected fragment. In the limit of large delay, the additional Coulomb energy from the second source is negligible and the energy measured is that of the original dissociation channel, (m, n), called the asymptotic energy, E_{asym}.

In principle, the molecular curves of both the (m, n) and $(m + i, n + j)$ channels are needed to fully predict the resultant kinetic energy of the fragments. We concentrate here on cases where $(2,0)$ is the initial channel, which has a low dissociation energy. Channels starting with fragments that are both ionized will dissociate significantly faster and, thus, will be harder to resolve in time. Assuming a purely Coulombic interaction for the subsequent double pulse channels, we can model the energy vs delay for various charge states. The total energy E_T as a function of delay is given by

$$E_T(\tau) = E_{asym} + \frac{(m + i)(n + j)}{r(\tau)}, \qquad (2)$$

where

$$r(\tau) = \tau v = \tau \sqrt{\frac{2E_{asym}}{m}}, \qquad (3)$$

and $r(\tau)$ is the internuclear separation at the second ionization step.

The energy of the $m + i$ fragment is measured and by changing τ we can determine the charge of the $n + j$ fragment. We have further assumed that the velocity during the time between the two pulses is constant and given by the final asymptotic energy. Ideally, E_{asym} can be measured from the single pulse TOF spectrum for the initial channel (m, n). However, we can also determine a strict lower bound on E_T, without knowing E_{asym}, by analytically minimizing E_T with respect to E_{asym} at each time delay. This process gives the theoretical minimum dissociation energy and will be useful below for identifying certain dissociation channels.

The experiment was performed using a Ti:sapphire laser system at a 1 kHz repetition rate with 400 μJ per pulse in 30 fs with a center wavelength of 800 nm [15]. The laser pulses are focused by an on-axis parabolic mirror in an ultrahigh vacuum chamber (base pressure $< 5 \times 10^{-10}$ torr). Iodine gas is introduced effusively at a typical pressure of 10^{-6} torr. A dc field extracts the ions through a 1 mm aperture and they are detected by a microchannel plate at the end of a TOF mass spectrometer. The grid voltages are set for symmetric velocity dispersion. Signals from the microchannel plate are amplified, discriminated, and counted by a computer. The absolute intensity is calibrated by fitting the Ar$^+$ ion yield (IY) to the Ammosov, Delone, Krainov (ADK) model [1,16]. Both the pump and probe pulses were

identical in polarization and pulse duration, only their intensities were varied.

Typical TOF spectra for I^{3+} are shown in Fig. 1. The pairs of single pulse peaks are unaffected by the presence of the double pulse as the intensities required to ionize these atomic charge states is too high. However, there is a new pair of low energy peaks between the $(3,1)$ pair and the zero kinetic energy peak (discussed below). As expected, the energy of the new peaks depends on pulse delay. Figure 2 shows the energy as a function of time delay from the I^{3+} TOF spectra for two different intensity ratios, 1:1 and 1:4, of the first to second pulse. For the 1:4 ratio, the data was fit to the energy vs delay model [Eq. (2)] for the $(3,1)$ channel with a fixed asymptotic energy of 0.8 eV. By measuring its asymptotic energy, the initial state of the $(3,1)$ channel was found to be the $(2,0)$ channel or, less likely, the $(1,0)$ channel:

$$I^{0+} + (I^{2+})^* + (\text{pulse 2}) \rightarrow I^{1+} + I^{3+}. \qquad (4)$$
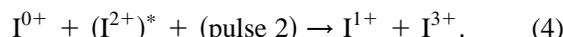
For the 1:1 ratio, however, it was not possible to fit the data to the energy vs delay model for the $(3,1)$ channel for any fixed asymptotic energy. Therefore, the theoretical minimum dissociation energy curve (described above) was calculated for the $(3,1)$ channel. The data were below this curve showing that it is kinematically impossible for the dissociation to have originated from a $(3,1)$ channel and must have come from the $(3,0)$ channel. The initial state of the $(3,0)$ channel was again found to have come from the $(2,0)$ channel by measuring the asymptotic energy [Eq. (1)]. In both of these cases the ionization of the I^{2+} fragment is unexpected as there is not sufficient intensity to ionize I^{0+} (1:1) or I^{1+} (1:4). Thus, the I^{2+} must be in an excited state.

Figure 3 similarly shows the energy as a function of time delay from the I^{4+} TOF spectrum. There are two peaks in the TOF spectrum that change energy as a function of time delay for the 1:4 intensity ratio. The data for one of the peaks was fit to the energy vs delay model for the
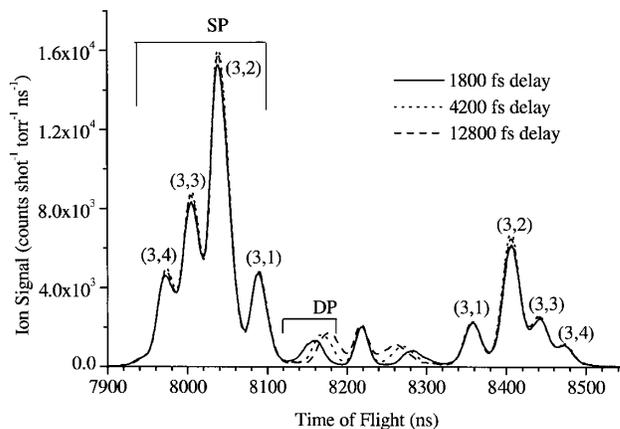
FIG. 1. Single pulse and double pulse TOF spectrum of I^{3+} for 1800, 4200, and 12 800 fs delays with 1:4 intensity ratio between the two pulses where the peak intensity of the pump pulse is 2×10^{14} W/cm^2.
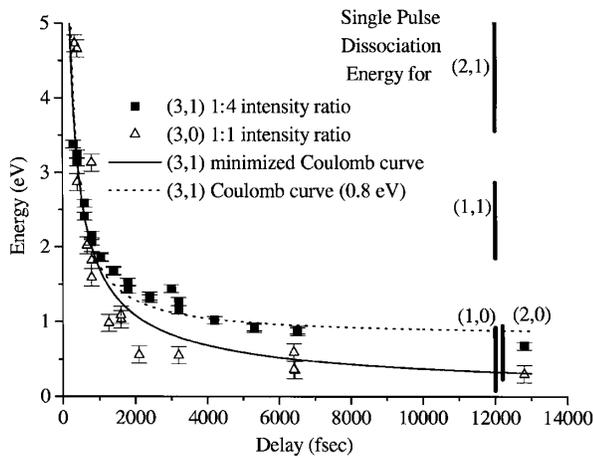
FIG. 2. I^{3+} energy vs delay for 1:1 and 1:4 intensity ratios where the peak intensity of the pump pulse is 2×10^{14} W/cm^2. Also included are the theoretical minimum dissociation energy curve for the (3,1) channel and a fit to the energy vs delay model for 0.8 eV. The single pulse dissociation energies found by analyzing the energy of the single pulse spectrum are also indicated here and in Fig. 3.

(4,1) channel with a fixed asymptotic energy of 0.5 eV. By measuring its asymptotic energy, the initial state of the (4,1) channel was again found to be the (2,0) channel:

$$I^{0+} + (I^{2+})^{**} + (\text{pulse } 2) \rightarrow I^{1+} + I^{4+}. \quad (5)$$

Finally, the data for the other peak in the 1:4 TOF spectrum was fit to the (4,2) channel for a fixed asymptotic energy of 0.6 eV. Asymptotic energy measurements again showed the initial state of the (4,2) channel to be the (2,0) channel:

$$I^{0+} + (I^{2+})^{**} + (\text{pulse } 2) \rightarrow I^{2+} + I^{4+}. \quad (6)$$

Since there is only enough intensity for $I \rightarrow I^{1+}$ or I^{2+}, the I^{2+} in Eqs. (5) and (6) must have started in a doubly excited state, $(I^{2+})^{**}$.
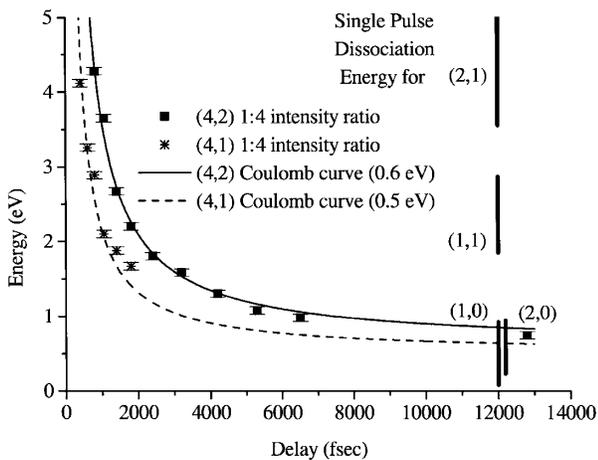
FIG. 3. I^{4+} energy vs delay for 1:4 intensity ratio for 1:4 intensity ratio where the peak intensity of the pump pulse is 2×10^{14} W/cm^2. The data are a fit to the energy vs delay model with 0.5 eV for the (4,1) channel and 0.6 eV for the (4,2) channel.

Figure 4 shows single pulse ion yield curves for the (1,1), (2,0), and (2,1) channels and the predicted I^{1+}, I^{2+}, and I^{3+} ion yields from the ADK tunneling ionization model. The IY curves confirm the previous analysis of the difference in final states produced by the 1:1 and 1:4 intensity ratios. For the purpose of this discussion, we will use the threshold values indicated by the IY curves. For the 1:1 ratio, the first pulse creates an initial (2,0) dissociation channel. The second pulse acts only on well separated atoms where the ionization rates are assumed to be described by the ADK tunneling ionization model. According to the ion yields, the second pulse is near the threshold to ionize neutral atomic iodine. Thus, it is likely that a significant fraction of neutral iodine will survive. Clearly, the second pulse is far below the threshold for ionization of I^{2+} in its ground state and, since I^{2+} is observed to ionize, I^{2+} must be in an excited state. For the 1:4 ratio, the first pulse again creates the (2,0) dissociation channel. The second pulse is now 4 times more intense and, hence, exceeds the threshold for ionization of I^{0+} and I^{1+}. This opens up the new channels $(2,0) \rightarrow (3,1)$ and $(3,2)$. $(2,0) \rightarrow (3,3)$ is still not accessible and $(2,0) \rightarrow (3,0)$ can no longer survive at this intensity. Similar results hold for the I^{4+} spectrum: $(2,0) \rightarrow (4,1)$ and $(4,2)$ are possible, but $(4,3)$ cannot be created. The remarkable fact here is that, while the I^{2+} ground state cannot be ionized, the original I^{2+} can doubly ionize to I^{4+}. Thus the original I^{2+} fragment must be doubly excited.

An estimate of the excitation energy for the $(I^{2+})^*$ and $(I^{2+})^{**}$ can be based on their anomalously low thresholds for ionization since I^{0+} acts as a probe for the intensity encountered by the I^{2+}. An exact estimate of the level of excitation is not possible using the ADK ionization model since ionization from an excited state is apparently not well described by this model [17]. However, the threshold intensity for a given ionization potential can be obtained by using the barrier suppression ionization (BSI) model [18]. A lower bound on the level of excitation of the I^{2+} in
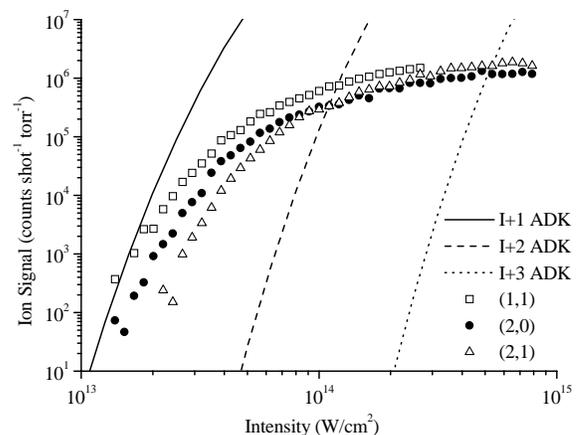
FIG. 4. Ion yields of molecular fragments (1,1), (2,0), (2,1) and theoretical ion yields for I^{1+}, I^{2+}, and I^{3+} based on the ADK tunneling model.

the $(2^*, 0) \rightarrow (3, 0)$ process can be made by assuming that the threshold intensity for $(I^{2+})^* \rightarrow I^{3+}$ is just below the threshold for $I^{0+} \rightarrow I^{1+}$. The BSI threshold intensity for the latter process is 4.7×10^{13} W/cm^2. In order to ionize at this same intensity, the $(I^{2+})^*$ must have a maximum binding energy of 18.0 eV. However, the binding energy for the ground state of I^{2+} is 33.2 eV, which means that the $(I^{2+})^*$ has an excitation energy of 15.2 eV. This excitation is well above the ground state configuration $5s^2 5p^3$ and may correspond to an excitation of the $5s5p^4$, $5s^2 5p^2 6s$, or $5s^2 5p^2 5d$ electronic configurations based on comparison with the Te^{1+} and Xe^{3+} isoelectronic species [19].

To estimate the excitation for the $(2, 0) \rightarrow (4, 1)$ case, we assume that the ionization is sequential and that the ionization rate of $(I^{2+})^{**} \rightarrow (I^{3+})^*$ is saturated compared to $(I^{3+})^* \rightarrow I^{4+}$. A lower bound on the level of excitation of the $(I^{3+})^*$ can again be made by assuming that the threshold intensity for $(I^{3+})^* \rightarrow I^{4+}$ is just below the threshold for $I^{1+} \rightarrow I^{2+}$. Using the same approximation as above, we find that the excitation energy of $(I^{3+})^*$ is 15.5 eV again corresponding to the $5s5p^3$, $5s^2 5p6s$, or $5s^2 5p5d$ electronic configurations which are well above the ground state configuration of $5s^2 5p^2$ [19].

By comparison, the field-free ground state excitation of asymmetric channels over symmetric channels is 8.7 eV for (2,0) over (1,1) and 14.1 eV for (3,1) over (2,2) [7]. In other words, the minimum energy of the initial molecular excitation in an asymmetric state is of the same order as the electronic excitation energy of the dissociated atom from that asymmetric state. Therefore, it appears that the excitation energy of the asymmetric over the symmetric state in the molecule has been transferred to electronic excitation in the dissociated molecule.

Amplified stimulated emission (ASE) from our multi-pass amplifier must be addressed as a possible cause for the secondary low energy peaks in the TOF spectrum. The low asymptotic energy of these peaks implies that the initial fragment channel must be (1,0) or (2,0). However, ASE can lead to low energy photodissociation of I_2 and could be the source of the secondary low energy channels. This is unlikely, as there would not be a clear dependence on the delay between the two 30 fs pulses if the initial dissociation was produced by the 100 ns ASE pulse. Nevertheless, to remove any question of the effect of ASE on the low energy double pulse peaks, we measured the TOF of I^{3+} using a constant amount of short pulse energy while varying the ASE energy [7] shown in Fig. 5. We know that the intensity of the short pulse is constant because the single pulse peaks depend only on the short pulse intensity. Any process that depends on ASE would change in the same way as the zero kinetic energy peak (which is known to result from ASE [7]). Going from a typical to a minimum amount of ASE, the zero kinetic energy peak is greatly reduced, whereas the single pulse and double pulse peaks caused from the short pulses are not affected, thus demonstrating that the double pulse peaks do not depend on ASE.
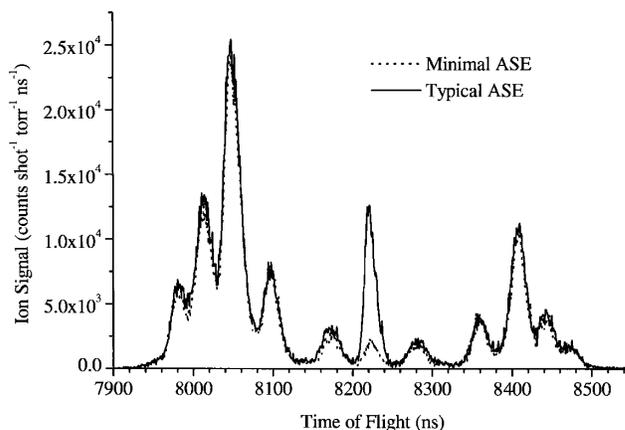
FIG. 5. TOF spectrum of I^{3+} for two levels of ASE with a peak intensity of the pump pulse is 2×10^{14} W/cm^2.

Using a new double pulse technique called correlated ion spectroscopy, we demonstrate that charge asymmetric dissociation leaves the fragments in singly or multiply excited electronic states. The observation of excited state fragments from dissociation imply an energy transfer from molecular excitation to atomic excitation. With a high branching ratio of 15%–30% for asymmetric states [7], the possibility exists for the direct efficient production of highly excited electronic states from a nonresonant laser pulse. Such production of excited states can potentially be used for VUV and soft x-ray lasers [20].

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