

## Direct evidence of the generality of charge-asymmetric dissociation of molecular iodine ionized by strong laser fields

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We present ion time-of-flight data showing strong-field ionization of iodine molecules up to  $I_2^{13+}$  using 33-fsec laser pulses. Every even molecular charge state shows an charge asymmetric dissociation channel ( $I_2^{2n+} \rightarrow I^{(n+1)+} + I^{(n-1)+}$ ) with a significant branching ratio (15–30%) in addition to the symmetric dissociation channel ( $I_2^{2n+} \rightarrow I^{n+} + I^{n+}$ ) showing the general nature of this process. Furthermore, all charge states are formed at internuclear separations less than the critical separation for electron localization and enhanced ionization ( $R_c$ ). One channel, in particular,  $I_2^{10+} \rightarrow I^{6+} + I^{4+}$ , represents a direct electronic excitation by nonresonant strong-field interaction to a state 20.9 eV above the ground state ( $I_2^{10+} \rightarrow I^{5+} + I^{5+}$ ). We show that the interaction of the dipole moment of the asymmetric charge distribution with the external field can account for this energy and the excitation mostly likely involves charge-transfer states. These results establish strong-field ionization of molecules as an efficient method for populating highly excited electronic states. [S1050-2947(98)01612-6]

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### I. INTRODUCTION

The existence and importance of charge-asymmetric dissociation (CAD) of molecular ions has been debated for quite a few years. Indications of asymmetric dissociation first came from early work on molecules analyzing ion time-of-flight (TOF) spectra, which measure the kinetic energies of the atomic ion fragments [1]. This work appeared, indirectly, at least, to show the presence of  $N_2^{2+} \rightarrow N^{2+} + N^{0+}$  and pointed out the significance of this process: charge asymmetric channels lie significantly higher in energy than the corresponding charge symmetric dissociation (CSD) channels (e.g.  $N_2^{2+} \rightarrow N^{1+} + N^{1+}$ ) and, thus, represent a direct excitation to highly excited electronic states of a molecular system through nonresonant multiphoton coupling. This new mode of excitation was soon corroborated by the observation of VUV radiation from electronic transitions in  $N_2^{2+}$  produced by strong field ionization, which had never been seen before [2], and opened up the possibility of accessing a whole new class of electronic excitations.

During this same period, several models were put forward for molecular ionization and dissociation in strong laser fields, which tended to predict charge symmetric dissociation [3,4]. Indeed, the evidence for asymmetric dissociation had come only from  $N_2^{2+}$  following UV excitation. Thus, it was possible that the dication was special, perhaps because it has metastable states that the higher-energy photons could access, and was not indicative of a more ubiquitous process. This possibility was more recently discussed [5], including asymmetric dissociation of  $I_2^{2+}$ . Although direct evidence for charge-asymmetric dissociation of more highly charged transient molecules ( $I_2^{4+} \rightarrow I^{3+} + I^{1+}$ ) was obtained [6], recent data showing that  $I_2^{3+}$  [5] has metastable states raises the possibility that the CAD of  $I_2^{4+}$  comes from a special precursor state of  $I_2^{3+}$  and, again, does not represent a more general process.

We present data consisting of ion TOF spectra of  $I^{1+}$  through  $I^{6+}$  with high resolution and dynamic range, which clearly demonstrate the large extent and importance of CAD channels. From the data we can identify the different dissociation channels and accurately determine their kinetic energy release, internuclear separation at ionization, and branching ratios into CAD and CSD channels. The branching ratios, in particular, represent a new challenge to models of multiphoton ionization (MPI) as they cannot be predicted from molecular barrier suppression ionization (BSI) models [5] and do not apply to the more extensively studied  $H_2^+$  molecule [7]. From our data we find that: (1) CAD in molecular iodine persists up to the highest even charge states observed:  $I_2^{12+} \rightarrow I^{7+} + I^{5+}$ ; (2) at 33 fsec both CAD and CSD channels are created at distances less than the critical distance,  $R_c$  for enhanced ionization due to electron localization [8]; (3) the energy for the excitation of the charge asymmetric states can come from the dipole interaction of the field with the asymmetric charge distribution.

From these observations, we conclude that CAD is indeed a quite general aspect of the behavior of molecules in strong laser fields and is associated with ionization at an internuclear separation less than  $R_c$  for electron localization. This explains why data taken with longer laser pulses ( $>100$  fsec) do not show CAD from higher charge states as these experiments are dominated by ionization at  $R_c$  [9]. In addition, we note that although CAD necessarily implies that an excited molecular state was formed, the reverse may not be true: CSD does not necessarily imply dissociation from the molecular ground state as one of the atomic fragments may be in an excited state. Indeed, it is energetically possible for a CAD channel to convert to an excited-state CSD channel while the molecule is dissociating. Thus, the branching ratio into CAD channels is only a lower bound on the rate of production of excited molecular states.

The electronic states involved with CAD are most likely

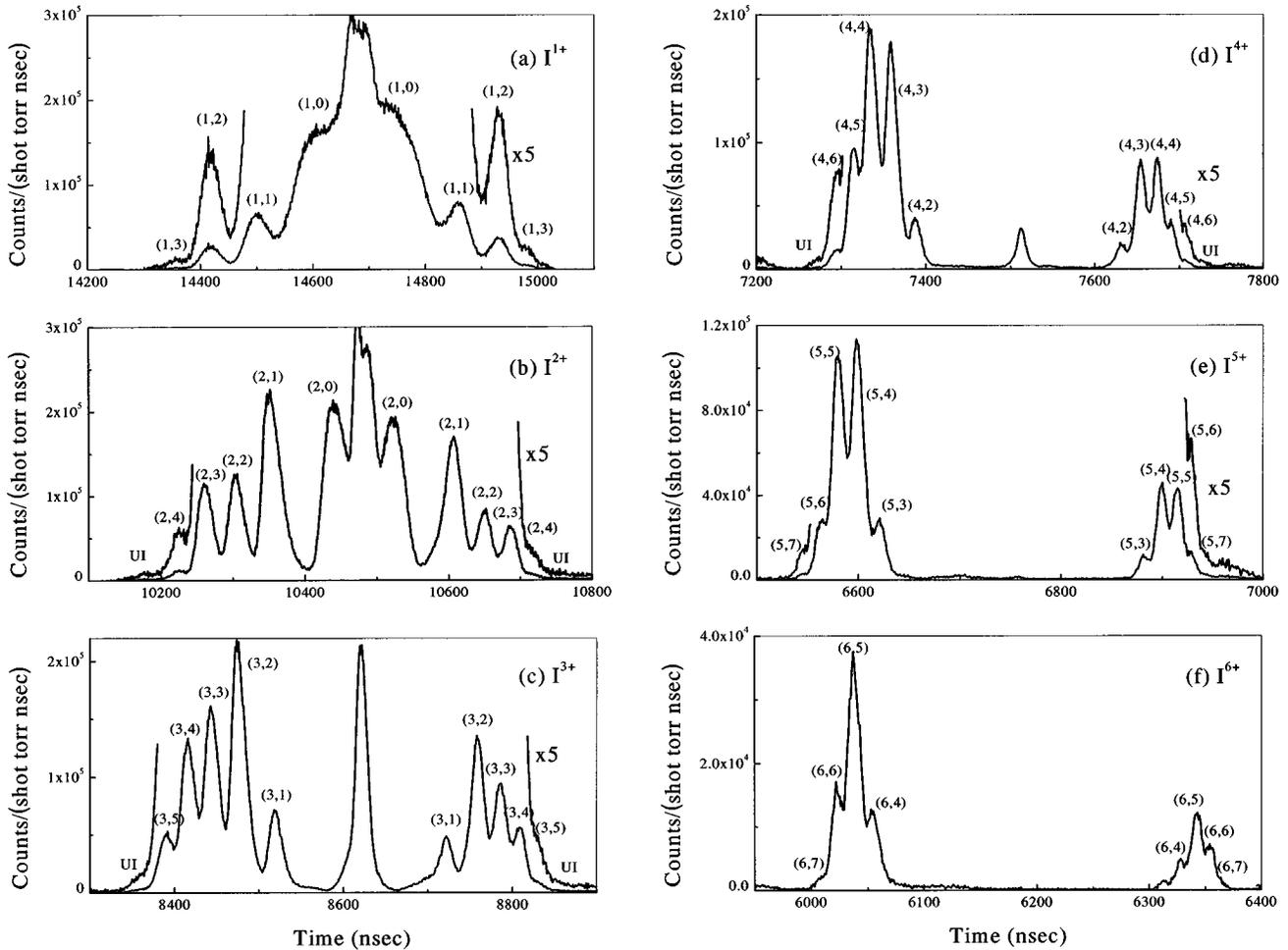


FIG. 1. Data for  $I^+$  through  $I^{6+}$  with an intensity of  $1.1 \times 10^{15}$  W/cm<sup>2</sup> at 33 fsec, with the dissociation channels labeled (UI: unidentified). The data in the wings of the spectra are also shown enhanced by a factor of 5.

the charge transfer states [6,10]. While it is not clear why such highly excited states are populated, the energy for the excitation appears to come from the interaction of the dipole moment of the asymmetric charge distribution with the strong laser field. If this is indeed true, the possibility arises that the excitation energy of electronic states that can be directly and efficiently populated with optical photons can be made arbitrarily large by simply increasing the laser intensity.

## II. EXPERIMENTAL CONFIGURATION

Our data for iodine were obtained with a high-repetition rate (1 kHz) ultrashort-pulse (33 fsec) Ti:sapphire laser system, consisting of an oscillator and ring multipass amplifier [11]. Energies of up to 400  $\mu$ J/pulse are obtained after pulse compression and focused by an on-axis parabolic mirror in a high vacuum chamber (base pressure  $< 5 \times 10^{-10}$  torr) to a maximum intensity of  $1.1 \times 10^{15}$  W/cm<sup>2</sup> for this experiment. The peak intensity was calibrated by fitting the ion yield of argon with a standard tunneling model [12] and was within a factor of two of the peak intensity calculated from the measured beam parameters. A fairly high-energy prepulse of ASE was present when the amplifier timing was optimized for maximum short-pulse energy. This results in some low

field photodissociation of the iodine molecules [13], leading to atomic iodine peaks with very low kinetic energy (Fig. 1). By injecting the seed pulse into the amplifier earlier in time we can minimize the ASE at the expense of short-pulse energy. Under conditions of low ASE the low-energy atomic peaks were greatly reduced (Fig. 2). However, the molecular dissociation peaks resulting from the strong field ionization were identical, as in Ref. [13]. The atomic peaks provide an additional check on the absolute laser intensity: an atomic

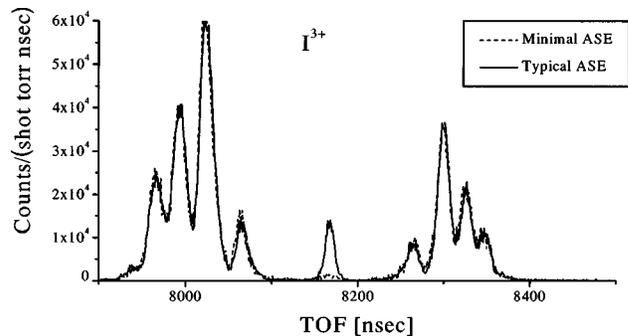


FIG. 2.  $I^{3+}$  spectrum showing that the ASE prepulse does not affect the dissociation channels. Note, the grid voltages on the TOF spectrometer and the laser intensity are different from Fig. 1.

TABLE I. Total dissociation energy of channel  $(q_1, q_2)$  in eV. Bold entries are charge asymmetric. The blank spaces indicate “not observed.”

$q_2/q_1$	1	2	3	4	5	6
0	0.7	<b>0.94</b>				
1	4.7	9.1	<b>13.2</b>			
2	9.3	17.1	25.6	<b>34.1</b>		
3	<b>14.0</b>	25.7	37.6	49.5	<b>61.1</b>	
4		<b>33.8</b>	49.5	65.6	80.4	<b>96.5</b>
5			<b>62.1</b>	80.8	100.0	119.5
6				<b>95.8</b>	119.6	141.8
7					<b>140.6</b>	164.1

BSI model [14] gives threshold intensities for the appearance of  $I^{4+}$  and  $I^{5+}$  of  $8.2 \times 10^{14}$  W/cm<sup>2</sup> and  $1.2 \times 10^{15}$  W/cm<sup>2</sup>, respectively, using the known ionization potentials of iodine [15]. This is consistent with our observation of atomic iodine only up to  $I^{4+}$ .

The iodine is introduced effusively from a stainless steel bulb containing solid iodine granules. Typical experimental pressures are around  $3 \times 10^{-7}$  torr. For the largest signals this corresponds to about 10 ions/shot, which makes space charge negligible. The ions are extracted by a dc electric field of 137 V/cm through a 1-mm pinhole, accelerated an additional 800 eV, and sent into a 45-cm field-free drift tube giving both symmetric velocity dispersion and high resolution [16]. Ions are detected with a microchannel plate, amplified, discriminated, sent to a multi-hit time-to-digital converter (TDC) and readout to a computer. The TDC has a time resolution of 0.5 nsec. The spectra have the usual symmetry about the arrival time of a zero-kinetic-energy ion with the two peaks representing ions with an initial velocity directed either towards or away from the detector. The latter can have a maximum kinetic energy of 100 eV per charge before striking the back grid. However, their collection efficiency is somewhat reduced over the forward directed fragments as they will have experienced more transverse spreading when they arrive at the extraction pinhole. Because of this, some of the channels are harder to measure in the late arriving peaks, but they are consistent with what would be inferred from the corresponding early peaks. For higher charge state fragments the relative collection efficiency also decreases for increasing initial kinetic energy.

### III. EXPERIMENTAL DATA

Figure 1 shows the ion spectra for charge states  $I^+$  through  $I^{6+}$  at an intensity of  $1.1 \times 10^{15}$  W/cm<sup>2</sup>. Each peak is identified by the specific dissociation channel:  $(m, n)$  corresponds to  $I_2^{(m+n)+} \rightarrow I^{m+} + I^{n+}$ , where the first number,  $m$ , designates the measured ion. Zero-kinetic-energy atomic ions are present up to  $I^{4+}$ , as discussed above. The separation of the early and late peaks gives the initial kinetic energy of the ions from which the total dissociation energy of each channel is determined, shown in Table I. These data are

TABLE II. Branching ratios into each asymmetric channel.

	(2,0)	(3,1)	(4,2)	(5,3)	(6,4)	(7,5)
33 fsec	0.32	0.22	0.15	0.19	0.21	0.17

somewhat redundant in that the energy of the (6,4) channel, for example, can be determined independently from both the  $I^{4+}$  (95.8 eV) or the  $I^{6+}$  (96.5 eV) ion peaks. All such pairs in the data agree quite well and this confirms the fact that space charge is unimportant as the different charge states would be affected differently. From Table I we can see that every even charge state up to  $I_2^{12+}$  has a measured asymmetric dissociation channel. The identification of the channels was checked using correlation techniques [17]. In addition to the labeled channels, high-energy peaks were seen in the  $I^{2+}$ ,  $I^{3+}$ , and  $I^{4+}$  data, which could not be identified through correlations because of the relatively weak signal strength. At present, we do not know their origin.

We use these data to measure branching ratios of a given charge state of a molecular ion into symmetric and asymmetric channels. For example,  $I_2^{6+}$  can dissociate into channels (3,3) or (4,2). We could simply take the ratio of these two signal strengths,

$$\alpha = S(4,2)/S(3,3), \quad (1)$$

where  $S(m, n)$  is the signal strength in the indicated channel obtained by fitting multiple Gaussian line shapes to the spectra, to determine the branching ratios

$$B(4,2) = \alpha/(1 + \alpha), \quad B(3,3) = 1/(1 + \alpha). \quad (2)$$

However, the redundancy of the data provides a more accurate determination. The uncertainty comes from the fact that  $S(3,3)$  is measured from the  $I^{3+}$  spectrum, while  $S(4,2)$  comes from the  $I^{2+}$  or  $I^{4+}$  spectrum and we would have to be concerned about relative efficiencies. However, these different spectra share common peaks that must be identical, i.e.,  $S(3,4)$  and  $S(4,3)$ . To exploit this fact, we normalize the signals as follows:

$$\alpha = [S(4,2)/S(4,3)]/[S(3,3)/S(3,4)]. \quad (3)$$

Furthermore, there is another independent measure of this ratio,

$$\alpha = [S(2,4)/S(2,3)]/[S(3,3)/S(3,2)] \quad (4)$$

and we average these separate measurements together. Measured in this way, the branching ratio does not have a strong intensity dependence except, of course, at threshold. These results are summarized in Table II.

Once the identification and energies of the dissociation channels are known, we can find the internuclear separation at which the dissociation started,  $R_{ion}$ , by assuming the total kinetic energy of the ion fragments is given by the Coulomb repulsion:

$$U = q_1 q_2 / R_{ion}. \quad (5)$$

These results are shown in Fig. 3.

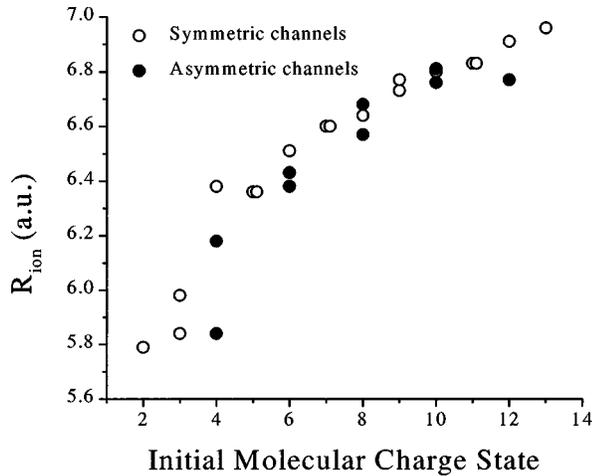


FIG. 3. Internuclear separation at ionization for symmetric vs asymmetric channels. For  $n \neq m$ ,  $R_{\text{ion}}$  is plotted for both the  $(n, m)$  and  $(m, n)$  channels.

#### IV. DISCUSSION

Having obtained data on high molecular charge states ionized inside of  $R_c$  we can test several aspects of strong field molecular ionization in a new limit. The first question concerns the highest charge state observed,  $\text{I}_2^{13+}$ . High molecular charge states are usually attributed to enhanced ionization rates at  $R_c$  [5]. However, this does not preclude the possibility of ionization inside of  $R_c$ . Posthumus *et al.*, [5] have presented a BSI model, which provides results for any internuclear separation. However, with long pulses the molecule invariably passes through  $R_c$  before the ionization has ended. In our case, we can test the model for high charge states without going through  $R_c$ . This model predicts a threshold intensity of  $1.4 \times 10^{15} \text{ W/cm}^2$  for the (6,7) dissociation channel at our measured internuclear separation of  $R_{\text{ion}} = 7.0 \text{ a.u.}$  Given the approximations of the model and the uncertainties in the determination of the intensity this agrees quite well with our peak intensity.

The smooth trend in the data in Fig. 3 confirms an earlier prediction by Codling *et al.* [3], which stated that as the charge state of the initial molecular ion increases, so does  $R_{\text{ion}}$ . This can be explained as follows: as the intensity rises to the point where ionization to the high charge state occurs, lower charge state transient molecules are formed, which begin to dissociate, so the internuclear separation is larger when the higher charge states are produced. This interpretation was first proposed for  $\text{N}_2$  [3], but fell out of favor because the predicted dissociation energy dependence on pulse duration failed to materialize experimentally [9] mainly because of enhanced ionization at  $R_c$ . However, our new observation of this smooth trend confirms this earlier picture because the ionization occurs before reaching  $R_c$ .

Finally, we can check whether sufficient energy is available in the dipole interaction of the asymmetric molecule with the laser field to excite the charge transfer states. The excitation energy of the lowest state leading to asymmetric dissociation can be estimated as follows (see Fig. 4): the energy difference between the dissociation limits of the  $(n, n)$  and  $(n+1, n-1)$  channel is given by  $I_p(n+1) - I_p(n)$ , where  $I_p(m)$  is the energy required to ionize

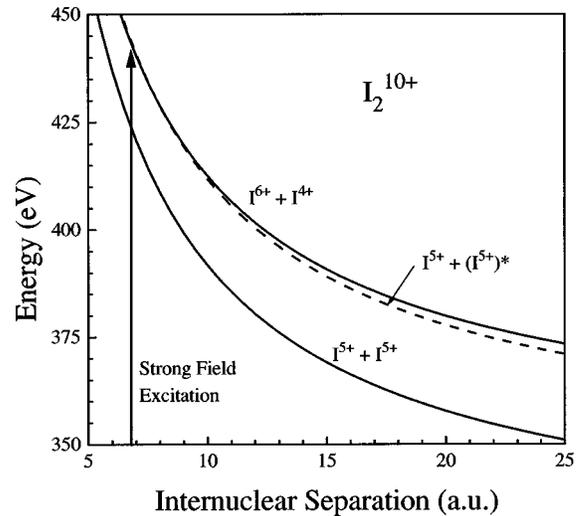


FIG. 4. Coulomb curves for  $\text{I}_2^{10+}$  showing the ground and excited state CSD curves as well as a CAD curve.

$\text{I}^{(m-1)+}$ . If we assume a purely Coulombic interaction between the ions, which is reasonable at these charge states, the total energy difference between the  $(n, n)$  and  $(n+1, n-1)$  curves at an internuclear separation,  $R$ , will be

$$\Delta E_n = I_p(n+1) - I_p(n) - 1/R, \quad (6)$$

in atomic units.

For our data, given the specific ionization potentials of iodine,  $\Delta E_n$  is the largest for  $n=5$ , i.e., the (6,4) vs the (5,5) states, and is 20.9 eV at the measured  $R_{\text{ion}} = 6.8 \text{ a.u.}$  From this we can determine the field required to access this state by setting

$$\Delta E_n = \Delta q R_{\text{ion}} F/2, \quad (7)$$

where  $F$  is the laser field strength in atomic units and  $\Delta q$  is the charge difference between the two ion fragments [6]. For the example above, solving for  $F$  gives  $F = 0.11 \text{ a.u.}$  corresponding to a laser intensity of  $4.5 \times 10^{14} \text{ W/cm}^2$ . The measured threshold for the (6,4) channel is  $5 \times 10^{14} \text{ W/cm}^2$ , which also agrees exactly with the molecular BSI intensity for the (5,5) channel. Thus, at the intensity required to produce  $\text{I}_2^{10+}$  the dipole energy is sufficient to excite the charge transfer state 20.9 eV above the symmetric ground state.

Once the excited charge asymmetric state has been populated, as the molecule dissociates, it will encounter curve crossings with excited charge symmetric states (Fig. 4). At that point, the molecule can pass adiabatically onto the charge symmetric curve and be counted as a CSD channel. For this reason, our measured branching ratio to CAD channels is only a lower bound.

#### V. CONCLUSION

We have produced molecular charge states of iodine up to  $\text{I}_2^{13+}$  using 33 fsec laser pulses at  $1.1 \times 10^{15} \text{ W/cm}^2$ . Every even charge state shows charge asymmetric dissociation with a substantial branching ratio. The level of ionization is consistent with molecular BSI while the energy required to ex-

cite the CAD curves can be obtained with the dipole interaction with the laser field. The highest degree of excitation observed was 20.9 eV in  $I_2^{10+}$ . This demonstrates that efficient highly specific excitation of electronic states is possible with nonresonant strong field ionization of molecules.

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