Multiple ionization of atomic and molecular iodine in strong laser fields

D. Normand and M. Schmidt

*Service des Photons des Atomes et des Molécules, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Saclay,
91191 Gif-sur-Yvette Cedex, France*

(Received 14 September 1995)

We compare the multiple ionization of atomic and molecular iodine using 100-fs laser pulses at 610 nm over a wide range of laser intensities (2×10^{12} W/cm^2–3×10^{15} W/cm^2). We show that the elongation of the molecular ion to a critical distance drastically enhances the multiple ionization probability of the molecule compared to that of the atom. In particular, the yield of the ten-times-ionized molecule is higher than that of the three-times-ionized atom around 10^{14} W/cm^2. This observation supports recent theoretical work on the role of the electron localization in intense-field molecular ionization. Around 10^{15} W/cm^2, the quintuple ionization of atoms is observed, whereas fast I^{2+} fragments arising from the I$_2$ Coulomb explosion are not further ionized, even with 300- or 500-fs laser pulses. This result supports the concept of molecule stabilization in strong laser fields.

PACS number(s): 33.80.Rv

When molecules in the gas phase are subjected to intense (sub)picosecond laser fields in excess of 10^{13} W/cm^2, they lose several electrons and the molecular ions explode into energetic fragments [1,2]. This process is known as multielectron dissociative ionization (MEDI). With a linearly polarized laser, diatomic molecules get aligned along the laser electric field ε [3,4] so that the fragments are emitted in sharp cones centered along the ε vector. Despite the inherent complexity of the processes involved, the MEDI studies have provided surprisingly simple outcomes, in particular the independence of the molecular explosion on the laser parameters, i.e., the wavelength, pulse duration, and intensity [5].

The experimental investigations performed on a large variety of molecules [5,6] suggest that the MEDI scenario proceeds in two steps: (1) The neutral molecules are doubly ionized at the equilibrium internuclear separation R_e, which starts up the molecular dissociation. (2) At a critical internuclear distance R_c, the double-charged molecular ions are multiply ionized, which triggers the Coulomb repulsion. This critical distance is found to be unique for all the fragmentation channels of a given molecule. In the case of chlorine [5], up to ten electrons are stripped from the molecule for a maximum laser intensity of 10^{15} W/cm^2; all the fragment energies correspond to an explosion of the molecular ions starting at $R_c = 2.9$ Å $= 1.4 R_e$. Concerning the dynamics of Coulomb explosion, recent experiments [5,6,7] suggest that the molecular ions are stabilized by the strong field at this critical distance R_c, and explode in the falling edge of the pulse.

The observation that the multiple ionization stages of a molecule are achieved at $R = R_c$ has been explained very recently by several theoretical works [8–11]. Using a simple field ionization model, Posthumus *et al.* [8] define a critical distance R_c and a critical field F_c for which the electron energy touches the field-lowered inner and outer potential barriers. The calculated and measured critical distances R_c are quite close for all studied molecules, but the model fails when describing the ion apparition intensities. A recent model [9] predicts a drastic enhancement of the molecule

ionization cross sections at R_c. In particular, for a laser intensity of 1.3×10^{14} W/cm^2, the ionization rate of a singly charged molecular ion at $R = R_e$ is found to be comparable to that of a seven-times-ionized molecule at $R = R_c$. Moreover, the calculations suggest that in the region close to R_c, ionization of diatomic ions is drastically enhanced compared to atomic ionization, since the electron can tunnel through the narrow internal barrier directly to the continuum. Parallel interpretations associate enhanced ionization with the effect of the static electric field from one nucleus acting on an electron localized close to the other nucleus.

The aim of the present paper is twofold. First, we compare directly the ionization probabilities of atoms and molecules to test whether the multiple ionization of diatomic ions at the critical distance R_c is indeed much more efficient than that of the atoms. Second, we show that the enhanced ionization probability of molecules at $R = R_c$ is compatible with the concept of *laser-induced molecular stabilization* [5,7], i.e., one or more valence electrons become "superexcited" at $R = R_c$, and the dissociation of the molecular ion is delayed until the end of the intense laser pulse.

The experiment is performed with 100-, 300-, and 500-fs pulses at a wavelength of 610 nm. The pulses are generated by a white-light continuum amplified by three dye amplifiers and focused with a $f = 60$ mm achromatic lens that yields a maximum intensity of 5×10^{15} W/cm^2. The mass spectrometer [5] is based on a 20-cm-long drift tube with a double acceleration chamber. The acceleration fields in the two chambers (100 and 400 V/cm, respectively) ensure that the ion times of flight (TOF) are linear with their initial axial velocities. The ions are received on an electron multiplier through a 3-mm pinhole and digitized by a numerical oscilloscope with a sampling interval of 1 ns. The laser polarization is held parallel to the detection axis. The ion energy measurements are made through the splittings of the ion peaks due to the alignment of the fragments along the laser polarization axis [3,4]. The I$_2$ gas pressure is adjusted whenever the laser intensity is varied, in order to keep the number of ions created roughly constant and to avoid space-charge
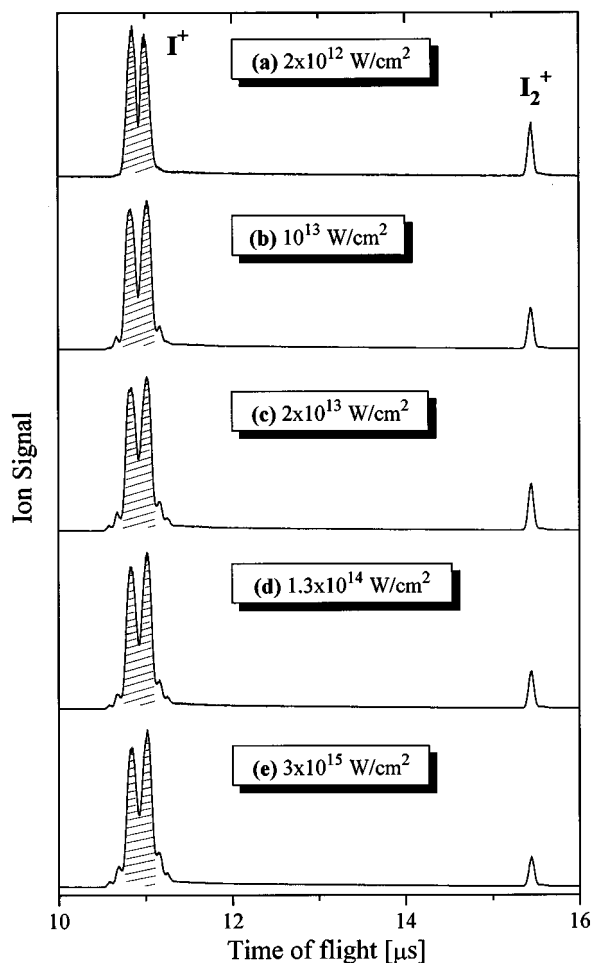
FIG. 1. TOF mass spectra showing the I^+ and I_2^+ ions created by multiple ionizations of atomic and molecular iodine. The data are recorded with 100-fs pulses at 610 nm, for a set of laser intensities ranging from 2×10^{12} to 3×10^{15} W/cm^2. The low-energy peaks (hatched) arise from the ionization of iodine atoms.
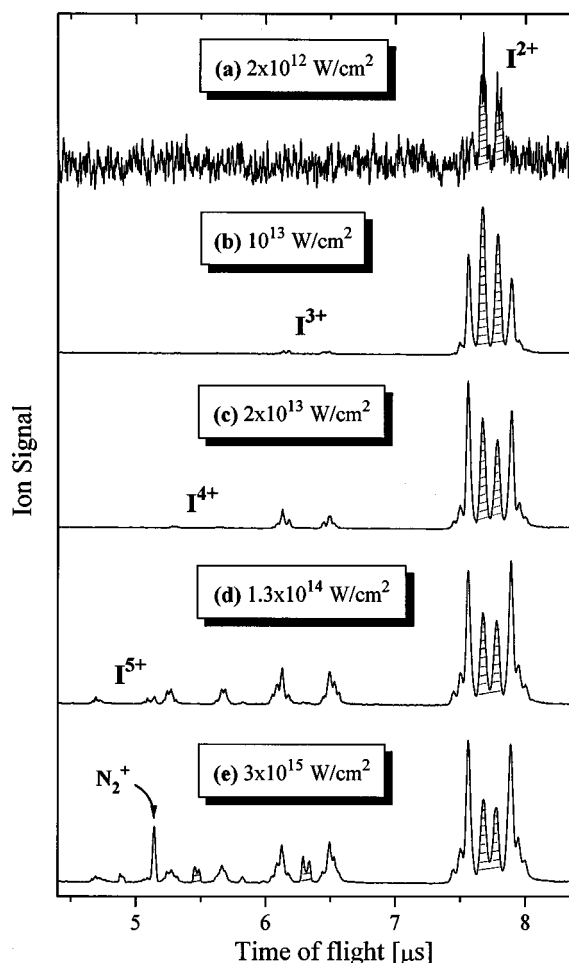

FIG. 2. TOF mass spectra showing the multiply charged ions created by multiple ionizations of atomic and molecular iodine. The data are recorded with 100-fs pulses at 610 nm, for a set of laser intensities ranging from 2×10^{12} to 3×10^{15} W/cm^2. The low-energy peaks (hatched) arise from the ionization of iodine atoms. The ion charge states are indicated in the figure.

effects. So doing, some parasitic signals such as N_2^+ (mass 28) or HCl^+ (masses 36 and 38) show up in the high intensity TOF spectra that are recorded at the lowest iodine pressure.

The TOF mass spectra recorded at five increasing laser intensities from 2×10^{12} to 3×10^{15} W/cm^2 are shown in Figs. 1 and 2. The spectra containing the singly charged ions are displayed in Fig. 1, whereas the multiply charged ions are shown in Fig. 2. At the lowest laser intensity investigated, we observe singly ionized I_2^+ molecular ions and I^+ atomic ions having 0.3 eV kinetic energy [Fig. 1(a)]. The atomic ions are due to the multiphoton ionization of neutral fragments arising from the photodissociation via the repulsive $B^1\Pi_u^+$ state of the neutral molecule at 610 nm, as well as from the predissociation of the bound $B^3\Pi_u^+$ state into $B^1\Pi_u^+$. The dissociation yields atomic fragments each having a maximum kinetic energy of 0.24 eV. The dissociative quantum yield of I_2 at 610 nm has been measured to be about 70% [12]. Photodissociation starts in the beginning of the laser-pulse pedestal at very weak intensities. Since the neutral fragments gain no electrostatic energy in the ionization process, they must be ionized at the end of the dissociation

process, at an internuclear separation of at least 100 Å. Accordingly, higher ionization stages will not significantly change the energies of these fragments. This atomic process is thus easily distinguishable from the molecular MEDI process in which the ionic fragments are strongly accelerated by the Coulomb repulsion. Figure 1(a) indicates that about 15% of the molecules have not been dissociated by the laser-pulse pedestal, which agrees reasonably well with previous results [12]. Due to the photodissociation process, the interaction volume consists of a uniform mixture of neutral atomic and molecular iodine. The residual molecules are subjected to the intense 100-fs pulse leading to MEDI via the channel $I_2^{(p+q)+}\rightarrow I^{p+}+I^{q+}$, further denoted by (p,q). In addition to the prominent I_2^+ and slow I^+ [0.3 eV] ions, nascent I^+ [2 eV] ions from the (1,1) MEDI channel [Fig. 1(a)] and slow I^{2+} [0.3 eV] ions are also observed [Fig. 2(a)]. The ionization potentials of the atomic $I^+\rightarrow I^{2+}$ and molecular $I_2^+\rightarrow I_2^{2+}\rightarrow I^+$ [2 eV]$+I^+$ [2 eV] processes are 19.1 and 25.5 eV, respectively [13,14]. At 2×10^{12} W/cm^2, the probabilities for double ionization of the iodine atoms and molecules at their equilibrium internuclear distance R_e are found to be comparable.

In the following, we compare the probabilities for multiple ionization of the atomic and molecular processes at the higher laser intensities. At 10^{13} W/cm^2, fast I$^+$ ions [Fig. 1(b)] and I^{2+} ions [Fig. 2(b)] show up. They proceed from the Coulomb explosion of I$_2^{3+}$ and I$_2^{4+}$ molecular ions via the (1,2) and (2,2) dissociative channels. At 2×10^{13} W/cm^2, the (3,3) and (3,4) channels are clearly detected [Fig. 2(c)]. Finally, for an intensity of 1.3×10^{14} W/cm^2, fast I^{4+} and I^{5+} ions issued from the (4,4), (4,5), and even (5,5) channels show up [Fig. 2(d)]. Note that the kinetic energies of the fragments correspond to an explosion of the molecule at the critical internuclear distance ($R_c=3.8$ Å), rather than at $R=R_e$ [6]. Interestingly, no trace of I^{3+} [0.3 eV] and of higher charged slow fragments is observed at this intensity level. Thus, at 1.3×10^{14} W/cm^2, up to ten electrons can be extracted from the iodine molecule, at the critical distance, but the atom cannot even be triply ionized. This experimental demonstration shows that the elongation of the molecular ion to the critical distance enhances drastically the multiple ionization probability of the molecule compared to that of the atom. This observation confirms the general predictions given in Ref. [9]. However, a disagreement remains between theory and experiment regarding the threshold intensities of the different dissociative channels. Indeed, the theory predicts that the threshold intensity for the double ionization of the molecule at $R=R_e$ should induce up to the seventh ionization of the molecule at $R=R_c$. The experiment demonstrates that the (p,q) channels show up one after the other as the laser intensity is gradually increased.

At the highest laser intensity investigated (3×10^{15} W/cm^2), a saturation of the molecular process is observed. Indeed, the fragment energies and the branching ratios of the (p,q) channels [Fig. 2(e)] are identical to that generated at 1.3×10^{14} W/cm^2. By contrast, the atomic process is strongly affected by the increase of the laser intensity. A series of slow multiply charged ions, i.e., I^{3+}, I^{4+}, and I^{5+} now show up in between the fast forward and backward ions. They all bear the same kinetic energy of 0.3 eV, which signs the multiple ionization of the I [0.3 eV] atoms. We conclude that the increase of the laser intensity compensates for the lower ionization rate of the atomic process, so that the probability for the fifth ionization of the iodine atom equals the probability for the tenth ionization of the molecule at $R=R_c$.

Finally, we discuss the implications of the present observations for the concept of *molecule stabilization in strong laser fields* [5–8]. This concept has been introduced on account of several experiments showing that (1) the MEDI dynamics do not depend on the laser-pulse duration, and (2) the fragments do not undergo postdissociation ionization (PDI), even with laser pulses as long as 2 ps. In order to further explore molecular stabilization, the experiment performed on atomic and molecular iodine with 100-fs pulses has been repeated with longer pulses. The Fig. 3 displays the TOF spectra showing the I^{2+}, I^{3+}, and I^{4+} ions obtained for pulse durations of 100 fs [Fig. 3(a)], 300 fs [Fig. 3(b)], and 500 fs [Fig. 3(c)]. Figure 3(a) corresponds to the spectrum already given in Fig. 2(e). The laser intensity is 2×10^{15} W/cm^2 in Fig. 3(b), and is reduced to 5×10^{14} W/cm^2 in Fig. 3(c), but this is sufficient to induce strong atomic ionization processes
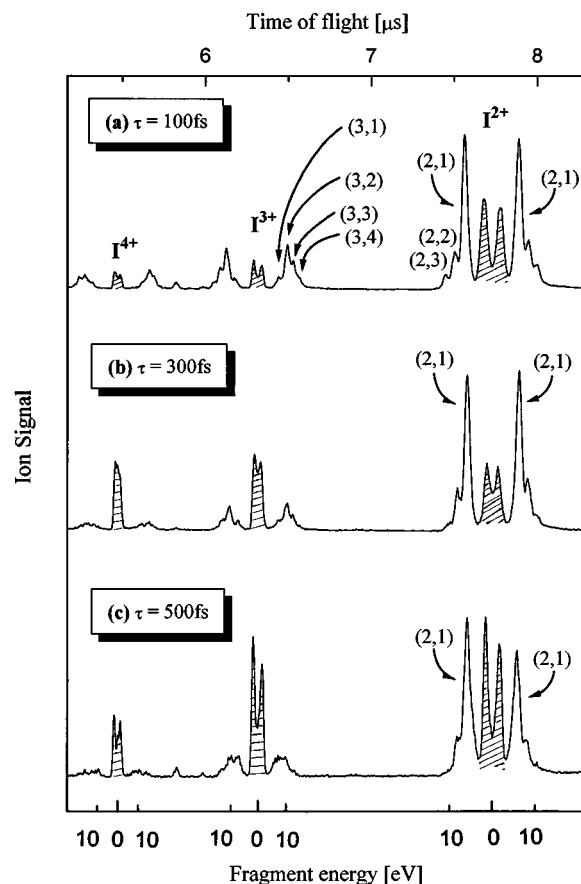

FIG. 3. TOF mass spectra showing the I^{2+}, I^{3+}, and I^{4+} ions created by multiple ionizations of atomic and molecular iodine. The spectra are recorded at 610 nm for different laser-pulse durations (a) 100-fs pulses at 3×10^{15} W/cm^2, $p(I_2)=2\times10^{-7}$ T; (b) 300-fs pulses at 2×10^{15} W/cm^2, $p(I_2)=4\times10^{-7}$ T; and (c) 500-fs pulses at 3×10^{14} W/cm^2, $p(I_2)=4\times10^{-6}$ T. The hatched peaks arise from the ionization of iodine atoms. The assignment of the fast ions to the (p,q) dissociative channels is also given.

(I$^{2+}\rightarrow$I$^{3+}\rightarrow$I^{4+}). Note that the dissociating ions have *a fortiori* an even higher ionization probability at internuclear separations between R_c and infinity [9]. By contrast, the parts of the spectra containing the I^{3+} peaks [Figs. 3(a)–3(c)] show *no signal big enough* to account for the PDI of the strong I^{2+} [4 eV] signal of the (2,1) channel. With ultrashort pulses, it could be argued that the heavy iodine is nearly "frozen" during the interaction and that all fragments arise from molecular ions created at the peak of the spatial intensity distribution; then the laser intensity drops rapidly, so that the PDI probability is negligible. However, with 300- or 500-fs pulses, the molecular ions should have time to dissociate during the slower rise time of the pulse. For example, the threshold intensity of the I$_2^{3+}$ molecular ions is about 3×10^{12} W/cm^2. With 300-fs pulses peaking at 2×10^{15} W/cm^2 [Fig. 3(b)] the I$_2^{3+}$ ions appear on axis 450 fs before the peak of the pulse. If the stabilization hypothesis is disregarded, these ions dissociate into I$^+$ and I^{2+} ions *before* the threshold intensity of the I$_2^{4+}$ ions is reached. The absence of PDI requires that the fast fragments not be present during the hot core of the laser pulse, but are created afterwards. The 300- and 500-fs experiments

therefore support the hypothesis of laser-induced molecular stabilization.

In conclusion, we have compared the multiple ionization processes of atomic and molecular iodine induced by intense 100-, 300-, and 500-fs laser pulses at 610 nm. We find that (1) the double-ionization cross section for atoms is comparable to that of molecules at their equilibrium internuclear distance; (2) the elongation of the molecular ion to a critical distance drastically enhances its multiple-ionization probability compared to that of the atom. For instance, ten-times-ionized molecules are created at a laser intensity for which the triply charged atomic ion is still not detected; (3) under conditions where the iodine atom is four-times ionized,

prominent I^{2+} MEDI fragments are not further ionized by the laser, even with 500-fs laser pulses. This last observation supports the concept of molecule stabilization in strong laser fields [5]. Indeed, the nonobservation of the PDI process, under conditions where its probability is very high [7], implies that the molecular explosion occurs in the falling edge of the laser pulse, when the laser intensity is too low to induce PDI.

[1] K. Codling and L. J. Frasinski, J. Phys. B **26**, 783 (1993), and references therein.

[2] A. Giusti-Suzor, F. H. Mies, L. F. DiMauro, E. Charron, and B. Yang, J. Phys. B **28**, 309 (1995), and references therein.

[3] D. Normand, L. A. Lompré, and C. Cornaggia, J. Phys. B **25**, L497 (1992).

[4] P. Dietrich, D. T. Strickland, M. Laberge, and P. B. Corkum, Phys. Rev. A **47**, 2305 (1993).

[5] M. Schmidt, C. Cornaggia, and D. Normand, Phys. Rev. A **50**, 5037 (1994).

[6] M. Schmidt, P. D'Oliveira, P. Meynadier, D. Normand, and C. Cornaggia, Int. J. Nonlinear Opt. Phys. **4**, 817 (1995).

[7] M. Schmidt, D. Normand, M. Lewenstein, and P. D'Oliviera (unpublished).

[8] J. H. Posthumus, L. J. Frasinski, A. J. Giles, and K. Codling, J. Phys. B **28**, L349 (1995).

[9] T. Seideman, M. Yu. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).

[10] T. Zuo, S. Chelkowski, and A. D. Bandrauk, Phys. Rev. A **48**, 3837 (1993); **49**, 3943 (1994).

[11] K. C. Kulander, F. H. Mies, and K. J. Schafer, in *Super-intense Laser-atom Physics, Nato Advanced Study Institute Series B: Physics,* edited by H. G. Muller (Plenum, New York, in press).

[12] L. Brewer and J. Tellinghuisen, J. Chem. Phys. **8**, 3929 (1972).

[13] J.-M. Paulus and J.-C. Abbé, J. Chim. Phys. **70**, 690 (1973).

[14] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).