Observation of Enhanced Ionization of Molecular Ions in Intense Laser Fields

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Using ultrashort pulse multiphoton ionization, we launch a wave packet in the $I_2{}^{2+}$ state that dissociates into the fragments I^{2+} and I. We measure its multiphoton ionization probability as a function of its internuclear distance with an intense delayed probe pulse. If the probe pulse is polarized parallel to the internuclear axis, we observe a peak in the ionization yield at a critical distance of 5–6 Å. No such enhancement is seen with perpendicular polarization in agreement with the model of enhanced ionization by electron localization. [S0031-9007(96)00323-7]

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Using vibrational wave packet techniques [1], we show that the intense field ionization rates are very sensitive to the separation of nuclei in a molecular ion and, therefore, to the distribution of internuclear separations in a plasma. The observed maximum in the ionization rate occurs around a critical internuclear separation. Our results are consistent with recent theoretical predictions [2–5] of enhanced ionization which identify the process as a result of electron localization and unrelated to resonances or Frank-Condon factors [2]. These theoretical studies were stimulated by multiphoton dissociative ionization experiments in which all ionic fragments appeared to result from ionization of molecules at a characteristic internuclear separation [6,7]. These experiments provide indirect evidence of enhanced ionization [8] although alternative explanations [6,9] exist. This paper provides direct experimental evidence of enhanced ionization.

Theory predicts that enhanced ionization occurs in the strong field (or tunneling) limit [2]. In molecular ions (as in double quantum wells) the ability of an electron to move between the two ions (wells) in response to an external laser field directed along the internuclear axis depends on the internal potential barrier between these ions. For a short internuclear distance (R) this barrier is below the ground state energy. To escape the molecule the electron experiences only one (external) barrier through which it may tunnel, just like in an atom. For a very large internuclear distance an electron cannot move easily from one ion to the other because of the large internal Coulomb barrier and the electron will be localized around the ions (wells). Again, to escape the molecule, an electron must tunnel through potential barriers that are atomiclike. Between these two cases is a critical internuclear distance (R_{cr}) where the electron is partially trapped by the internal barrier until the field is large. Then, as illustrated in Fig. 1(a), the electron needs only tunnel through a small internal barrier in order to escape the molecule. Tunneling from the uphill atom [Fig. 1(a)] directly to the continuum is a new ionization pathway ensuring that the ionization rate of the molecular ion is greatly enhanced as compared with larger or smaller internuclear separations [10].

A quantitative description of enhanced ionization for $R > R_{\mathrm{cr}}$ is provided by a simple modification of atomic tunneling models [11]. In this description, enhanced ionization is due to an “enhanced field” experienced by the localized electron. That is, the laser field ($\vec{E}_L$) is augmented by the field ($\vec{E}_I$) of the adjacent atomic ion. [For example, 3 Å away from a doubly charged atomic ion (the approximate distance to the peak of the internal barrier for $R \sim 5$ Å) the Coulomb field is 3.2×10^8 V/cm. This is comparable to the peak field of an optical pulse with intensity of 1.3×10^{14} W/cm^2.] The resulting ionization rates can be determined [2] using a total field $\vec{E}_T = \vec{E}_L + \vec{E}_I$ in atomic models [11].

If the laser electric field is perpendicular to the molecular axis, the electron experiences only a single well structure in the field direction. Ionization is then almost atomiclike [Fig. 1(b)] for all internuclear separations. Reporting a maximum in the ionization rate for parallel polarization and a rate almost independent of the internuclear distance for perpendicular polarization is the main aim of this paper.

The experiment can be outlined as follows. First, iodine molecules are irradiated with an intense, 80 fs, visible laser pulse producing, among other things, some $I_2{}^{2+}$ molecular ions dissociating in the fragments I^{2+} and I (later called I^{2+}-I). Next, a temporally delayed laser pulse can further ionize this molecular ion. Last, the final charge state distribution is determined by the time-of-

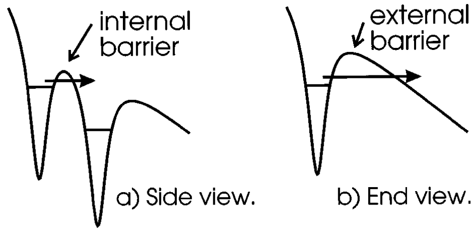

FIG. 1. Schematic of the potential curve for an electron in a diatomic molecular ion around the critical distance in an intense laser field polarized (a) along the internuclear axis or (b) perpendicularly to it.

flight (TOF) spectrum of the iodine ions. By observing the depletion of the I^{2+}-I final state and the simultaneous appearance of I^{2+}-I^{+} fragments as a function of the delay between the two pulses, we can study the dependence of the ionization rate of the I^{2+}-I molecular ion on its internuclear distance.

The experimental setup has been reported in detail elsewhere [12]. The output of an amplified colliding-pulse mode-locked laser (80 fs FWHM, 625 nm, 200 μJ, 10 Hz) is split in two similar pulses in a Michelson arrangement inducing a time delay between the pump and probe pulses. A zero order quarter-wave plate can be inserted in one of the Michelson's arms in order to rotate the polarization of the probe pulse. The zero delay is determined by cross correlation in a 100 μm thick KDP crystal. The two beams are focused by a $f = 1$ m lens $(f/66)$ onto a 200 μm diameter pinhole. This pinhole ensures good spatial overlap of the two beams. It is imaged with a 5-cm-focal-length on-axis parabolic mirror to a focal spot diameter of ~ 10 μm inside an ultrahigh-vacumm chamber [12] filled with $\sim 4 \times 10^{-7}$ Torr of room temperature molecular iodine. The pump and probe pulses have the estimated peak intensities of 2.4×10^{14} and 1.6×10^{14} W/cm^2.

The ions produced by laser irradiations are analyzed in a TOF mass spectrometer [12] that is designed to detect only ions having their velocity aligned with the TOF axis (acceptance angle of 11° for the I^{2+} ions originating from I^{2+}-I). The TOF of any ion is a signature of its charge/mass ratio and its initial kinetic energy [12].

In selecting a wave packet for study we are obliged to use a slow moving wave packet so that its motion can be time resolved with our 80 fs pulses. Slow wave packets are observed in the dissociation of I_2, ${I_2}^{+}$, and ${I_2}^{2+}$. We are also obliged to probe the wave packet with a strong field to reach the tunnel ionization limit in which enhanced ionization is predicted to occur. Finally, to simplify the interpretation of our experimental results, we use a probe pulse that is weaker than the pump pulse. Then, the presence of the probe pulse induces little modification to the kinetic energy spectrum for long delays. Among the three possible charge states on which a slow wave packet can be launched, only ${I_2}^{2+}$ dissociating in I^{2+} and I is created at high enough intensities [13] to approximately satisfy tunneling requirements.

In Fig. 2 we show the kinetic energy spectra for the I^{2+} ions at different delays between the pump and probe pulses, both polarized parallel to the TOF axis. The directional selectivity of the spectrometer ensures that the detected ions originate from molecules aligned along the laser field. The peaks in the spectra [13] are due to I^{2+} ions originating from the I^{2+}-I and I^{2+}-I^{+} final states (in order of increasing energy).

There are two conspicuous delay dependent changes in this series of spectra. First, the I^{2+}-I signal is strongly suppressed as the delay is increased from 0 to 166 fs and reappears as the delay is further increased. Second, a structure appears on the low energy part of the prominent I^{2+}-I^{+} peak around the 166 fs delay (labeled by an arrow on the 166 fs spectrum). For larger delays this structure moves toward lower energies and its amplitude decreases. It disappears for delays longer than 400 fs. These two main observations suggest that a significant fraction of the molecules dissociating via the I^{2+}-I channel is transferred to the I^{2+}-I^{+} channel due to strong field multiphoton ionization induced by the second laser pulse for a delay of $\sim$166 fs. For either shorter or longer delays, corresponding to smaller or longer internuclear distance in the I^{2+}-I wave packet, the ionization process is much less efficient. These are the general characteristics predicted for enhanced ionization.

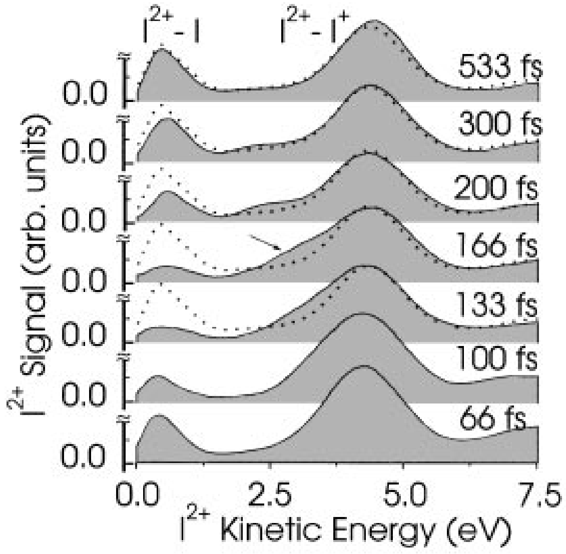

FIG. 2. I^{2+} kinetic energy spectra for different pump-probe delays. Both laser pulses are polarized along the internuclear axis. The dashed curve superimposed is the spectrum obtained for a delay of 1 ps. The arrow indicates the position of the I^{2+}-I^{+} moving structure at a delay of 166 fs. Each spectrum is an average of 2000 laser pulses. In order to emphasize the low energy features, the spectra are not corrected for detection efficiency (all signals should be multiplied by their kinetic energy).

The 80 fs pulses are too long to allow a full quantitative analysis of the moving structure. The kinetic energy where it appears and its subsequent evolution indicates that it is due to an I^{2+}-I^{+} molecular ion created by the probe pulse at an internuclear separation that increases with the delay. Such a structure can only originate from ionization and not from electronic rearrangement since the I^{3+}-I ion does not exist.

For small delays, the moving structure can result from ionization of the I^{2+}-I wave packet but also from ionization of a wave packet launched on the I^{+}-I^{+} potential. Our data are consistent with the fact that more than one wave packet can contribute to the moving structure since the magnitude of the moving structure exceeds the I^{2+}-I depletion at small delays.

At larger delays (>233 fs), the kinetic energy of the I^{2+}-I^{+} moving structure is less than the dissociation energy of the I^{+}-I^{+} wave packet. Thus, ionization of I^{+}-I^{+} cannot contribute to this structure. The decrease in the magnitude of the I^{2+}-I^{+} moving structure in Fig. 2 shows that, no matter what pathway leads to I^{2+}-I^{+}, ionization becomes less efficient at large internuclear separations.

We now concentrate on the depletion of the I^{2+}-I wave packet. This wave packet contains many energy components corresponding to different dissociation velocities. Figure 3 shows the magnitude of the signal corresponding to a fast component asymptotically moving at 24 Å/ps (0.94 eV) and a slow component moving at 10 Å/ps (0.16 eV) as a function of the pump probe delay. Both the components show a clear depletion around 166 fs and then recover to the same value that we find with no probe pulse. The fast part is depleted before the slow one and recovers before. [Although not shown here, the evolution of the central part of the I^{2+}-I signal (0.7 eV) falls between the two others.] This is in agreement with the concept of a critical distance $R_{\rm cr}$. Any component needs some time to reach $R_{\rm cr}$. The fastest dissociating component reaches $R_{\rm cr}$ before the slowest one and also leaves it first.

Data obtained with delays smaller than 100 fs are affected by the temporal overlap of the two pulses. Assuming an 80 fs FWHM pulse duration (autocorrelation trace and fit are shown in the inset of Fig. 3), it is only for delays larger than 100 fs that there is a local minimum between the two pulses for every phase. For smaller delays destructive interference will lead to "two pulses" while constructive interference will create a "single intense long pulse." Since our Michelson interferometer does not have an interferometric stability, all interference conditions are obtained and the results recorded at these small delays are an average of all phases. However, all charge states experience these fluctuations. Selecting a charge state to normalize our data leads to only small quantitative changes to Fig. 3.

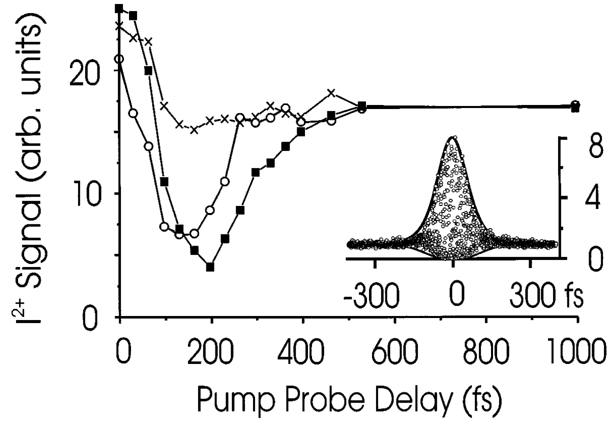

FIG. 3. Evolution of a fast (○) and slow (■) part of the I^{2+}-I wave packet for both laser pulses polarized along the internuclear axis and evolution of the central part (scaled by 2) of the I^{2+}-I wave packet for a probe polarized perpendicular to the axis (×). The inset shows the autocorrelation of our pulses fitted with the autocorrelation of an 80 fs hyperbolic secant shaped pulse.

We can estimate the critical distance by measuring the energy of the I^{2+}-I^{+} moving structure at 166 fs since it is a function of the internuclear distance and the dissociation velocity of the molecular parent ion [12]. Assuming that the average asymptotic dissociation velocity, $V_\infty = 20.6$ Å/ps (obtained with spectra corrected for the energy dependence of the detection efficiency) has been reached before 166 fs, the critical distance, determined as in [12], is 5.7 Å. This value agrees with a rough estimate of the evolution of the I^{2+}-I internuclear distance $R = R_0 + V_\infty t = 6.1$ Å (where $R_0 = 2.67$ Å is the equilibrium internuclear separation and $t = 166$ fs). We cannot be more precise because of the lack of knowledge of the potential structure and the limited temporal (spatial) resolution of our experiment.

As discussed in [2], $R_{\rm cr}$ is approximately the internuclear distance where the maximum of the internal potential barrier equals the ground state energy of the electron. This is the distance where the electron starts to be partially trapped by the internal barrier. The ground state energy is approximately given by the ionization potential of a single iodine atom (10.45 eV) plus the shift [$\sim 29/R$ (eV)] of the energy of the I^{+} well due to the I^{2+} neighbor ion. This condition yields $R_{\rm cr} \sim 5.3$ Å in good agreement with our measurement.

A direct comparison of the depletion of the I^{2+}-I signal around 166 fs (depleted by 70% of the asymptotic population) and at 400 fs (15% ± 5%) gives a lower bound of ~7 in the difference in ionization rate as R changes from ~5.5 to ~9 Å. This is a lower bound because we assume that the probe pulse makes no contribution to the I^{2+}-I signal by ionizing lower charged species at the delay of 166 fs. The probe is not so weak that this condition is certain.

The concept of enhanced ionization requires that the laser polarization is along the internuclear axis. To check, we recorded spectra under essentially the same experimental conditions as in Fig. 2 except that the polarization of the second pulse was perpendicular to the molecular axis. No clear suppression of the I^{2+}-I signal and no I^{2+}-I^{+} moving structure could be seen. Even increasing the intensity of the probe pulse by 50% produced no observable time dependent moving structure in the spectra. Figure 3 shows the evolution of the population of the central component of the I^{2+}-I wave packet for a probe perpendicular to the internuclear axis. This evolution clearly differs from the evolution obtained with parallel polarization: no observable enhancement of ionization rate occurs if the laser field's polarization is perpendicular to the internuclear axis.

All results are consistent with the predictions of the enhanced ionization model. However, some isolated results might have an alternative explanation. The decrease of the I^{2+}-I^{+} time dependent structure could, in principle, be due to a torque [14] on the molecular ions induced by the second pulse that would tend to align the fragment trajectories of the most polarizable ions with the field and therefore increase the detection efficiency. Since the polarizability decreases (from molecular polarizability to atomic polarizability) when the internuclear separation increases, the number of detected ions would decrease with the delay. As a direct test of the influence of the torque, the experiment was repeated with the probe pulse polarized at 45° to the TOF axis. If the polarizable molecules were ejected along the laser polarization this should reduce the detected signal for small delays and have no effect at large delays, qualitatively modifying the temporal evolution of the I^{2+}-I^{+} moving structure. Instead, we observed results almost identical to those in Fig. 2. Thus, molecular reorientation does not significantly contribute to the observed results.

In principle, the I^{2+}-I depletion around 166 fs could arise because of electronic rearrangement between excited channels of the ${I_2}^{2+}$ molecular ions. In particular, charge transfer coupling between states leading to the I^{2+}-I and I^{+}-I^{+} channels transfers one electron from one ion to the other, depleting I^{2+}-I and populating the I^{+}-I^{+} channel. Since it would lead to an equilibrium between the two populations, this coupling could partially explain the observed depletion of the I^{2+}-I channel. However, it could explain neither the simultaneous appearance of the moving I^{2+}-I^{+} nor the strength of the depletion.

Charge transfer coupling may have a role to play in enhanced ionization. Rather than depleting the I^{2+}-I channel by populating the I^{+}-I^{+} channel and subsequently decoupling these two channels because of slow nuclear motion, it is more likely that we transfer population from the I^{+}-I^{+} channel to the I^{2+}-I channel where it is rapidly depleted by enhanced ionization. This ionization pathway for the charge symmetric state has not yet been addressed theoretically.

The results of this paper demonstrate that multiphoton pump-probe spectroscopy of dissociative molecular ionic states is possible. During ionization (with the pump pulse) we also populate metastable states of molecular ions. This should launch vibrational wave packets. Following methods developed for neutral molecules [15], pump-probe spectroscopy could allow the spectroscopic constants of these states to be determined. This new approach to the spectroscopy of the molecular ions could complement existing techniques [16].

Enhanced ionization opens new directions in other areas of physics. The sensitivity of the ionization rate to internuclear separations is due to the importance of the local field of the adjacent ion. The local field experienced by an atom or ion can be controlled by placing it initially either alone, in a molecule, in a cluster, or in a plasma. These initial conditions with determine, and greatly modify [17], the ultimate charge states that the atomic fragments will reach after intense laser field irradiation. This also gives a way to shape plasma densities at will. For instance, molecules placed in the interference pattern of a laser field, having a frequency adequate for photodissociation, would dissociate only in regions of constructive interference, thereby creating alternate layers of atoms and molecules. Subsequently, irradiation with an intense pulse will turn them into layers of plasma with different densities that could be used as gratings or mirrors for high intensity, VUV or x rays, radiations.

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