Intense Field-Matter Interactions: Multiple Ionization of Clusters

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(Received 22 April 1996)

We report the results for the production of highly charged atomic species (e.g., Xe^{20+}, Kr^{18+}, O^{5+}, and C^{4+}) resulting from the interaction of intense laser fields (up to $\sim 10^{15}$ W/cm^2) with atomic and multicenter molecular clusters. The processes are also investigated using ultrafast pump-probe techniques, showing distinct beating patterns for the ionization structure in the molecular system. A comparison of our results with predictions of several different theoretical models provides strong support for the ionization ignition mechanism. [S0031-9007(96)01396-8]

PACS numbers: 36.40.Wa, 33.80.Rv

Elucidating processes initiated by the absorption of photons from femtosecond lasers is a subject of extensive current interest [1]. The study of the interaction of atoms, molecules, and clusters with high intensity laser fields is also made possible because of the strong fields generated by ultrafast lasers. Investigations [2–4] have revealed that sufficiently intense interactions with clusters can lead to multiple ionization events, and many questions have been raised as to the mechanisms involved. Several theoretical models have been devised from the results of earlier observations of multiple electron ejection. These include above threshold multiphoton ionization [5], barrier suppression ionization [6], and tunneling ionization [6,7], all of which have been unable to account for the high charge states observed in many experiments, in particular, ones involving the interactions of intense fields with van der Waals and hydrogen-bonded clusters [2–4]. To the best of our knowledge, the experiments [2,3] in our laboratory were the first to measure the large values of kinetic energy release in such highly charged clusters and provide the first direct observations for the mass-to-charge ratio of atomic ions ejected from clusters with charge states of large magnitude, although experiments by Rhodes and co-workers have observed the emission of x rays following the interaction of molecular beams of rare gases irradiated with intense laser fields [8]. To account for the high charge states observed in experiments involving clusters, a mechanism based on the coherent motions of the field ionization electrons has been proposed [4]. Alternatively, an ionization "ignition" mechanism has been formulated for laser-driven clusters [9].

In order to examine these two models, we conducted experiments on the interaction of clusters of several chosen classes with intense laser fields: namely, two atomic systems, xenon and krypton, and one molecular system, acetone. Pump-probe studies were conducted to investigate the time evolution of the formation of the multicharged fragments produced from a molecule with multiple atomic centers. Significantly, a "beating pattern" is seen in the case of the oxygen and carbon atomic ions generated from acetone. The resultant highly charged van der Waals or hydrogen-bonded clusters undergo Coulomb explosion and we observe multicharged atomic ions with charge states as high as Xe^{20+}, Kr^{18+}, C^{4+}, and O^{5+}.

The apparatus used in this study is a reflectron time-of-flight (TOF) mass spectrometer coupled with a femtosecond laser system which has been described in detail previously [10]. Briefly, a colliding pulse mode-locked ring dye laser, pumped by a CW argon ion laser, generated a 90 MHz pulse train with pulses 100 fs in duration and centered around 624 nm. The pulses are first amplified with a six pass bowtie amplifier, and subsequently amplified by an array of three prism dye cells (2, 6, and 12 mm bore). All of the amplification stages are pumped by the second harmonic (532 nm) of a 10 Hz Nd:YAG laser. The amplified femtosecond laser output is typically 2.5 mJ/pulse with a pulse duration of about 350 fs, as measured by a slow scan Michelson interferometric autocorrelator, which also serves as the delay stage in the pump-probe experiments.

For the studies of xenon and krypton, the sample gas at $\approx$100 torr, seeded in $\approx$2000 torr of helium, was expanded into a vacuum chamber, and the resultant monomer and cluster species were ionized by a femtosecond laser with an intensity of $\approx 1 \times 10^{15}$ W/cm^2. A time-of-flight spectrum of the multicharged xenon species is shown in Fig. 1. Species as highly charged as Xe^{20+} can clearly be seen. Even more highly charged species may be present, but the broad isotope distribution of xenon does not allow for their unambiguous identification. Figure 2 is a time-of-flight mass spectrum of the multicharged krypton species. It is important to note that the highly charged krypton atoms are observed only when trace amounts of hydrogen iodide are added to the gas sample, as discussed below. Charge states of up to Kr^{18+} have been observed but only species up to Kr^{17+} can clearly be seen in Fig. 2. Similarly, the broad isotope distributing of krypton does not allow for clear identification of any higher charged species.

For the study of acetone, the clusters were generated by bubbling helium through a vessel containing acetone, and introducing the acetone/helium mixture (at approximately 2000 torr) into a vacuum chamber. The acetone monomer

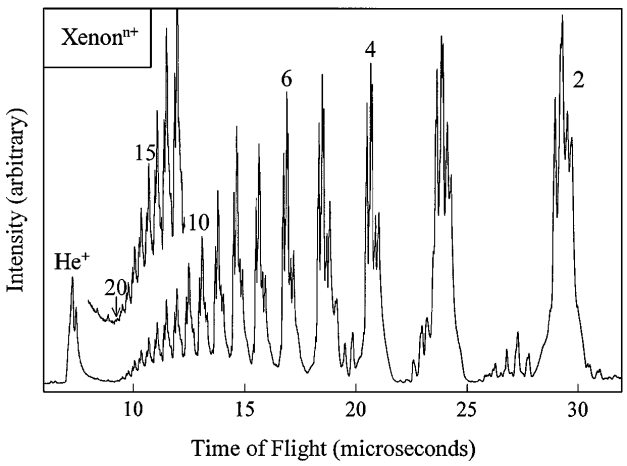

FIG. 1. Time-of-flight mass spectrum of multicharged xenon atoms, ionized at 624 nm. Atoms with charge states up to Xe^{20+} are clearly observed.

and clusters were ionized by a femtosecond laser in a pump-probe arrangement. The pump laser has a power density of $\approx 3 \times 10^{14}$ W/cm^2, and the intensity of the probe laser is slightly ($\sim 10\%$) less. The pump-probe transients of the oxygen fragments (O^{n+}, $1 \leq n \leq 5$) are shown in Fig. 3. There are several significant features that should be noted. A large dip is observed in the O^+ transient at zero delay, and a peak begins to grow in for each subsequently higher charged species. For the higher charged species (O^{n+}, $2 \leq n \leq 5$), the ion signal drops to a local minimum, then returns to a local maximum at some pump-probe delay. At longer delay times, the O^{n+}, $3 \leq n \leq 5$, show clear signs of a beating pattern. The unequal intensities of the maxima at positive and negative delay times can be attributed to the unequal pump and probe intensities, but significantly, the maxima in O^+ and O^{5+} occur at positive delay times, whereas the maxima in O^{2+}, O^{3+}, and O^{4+} occur at negative delay times.

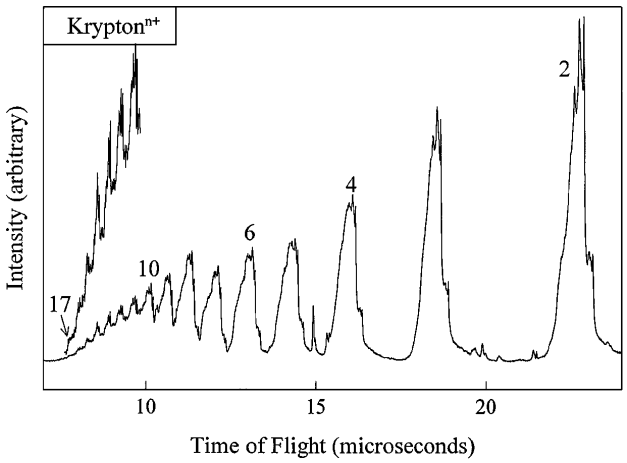

FIG. 2. Time-of-flight mass spectrum of multicharged krypton atoms, ionized at 624 nm. Atoms with charge states up to Kr^{17+} are clearly observed.

Although not shown, carbon fragments (C^{n+}, $1 \leq n \leq 4$) behave in a similar fashion.

The two recent models proposed to explain the high charge states obtained when irradiating clusters with high intensity ultrafast lasers are the coherent electron motion model (CEMM) [4] and the ionization ignition model (IIM) [9]. In the CEMM, the field-matter interaction can enter a regime of strong coupling in which the rate of multiple electron ejection can become comparable to the removal of a single electron. The enhanced coupling arises from the coherent motion of the field ionization electrons, behaving as a quasiparticle with a charge Ze and mass Zm_e; subsequent removal of electrons occurs in a fashion similar to electron impact ionization. The environment of a cluster provides a source of many electrons to participate in the coherent motions essential to the ionization process. In the IIM, the electrons are treated classically in the combined fields of the ion cores and the laser. After the initial ionization events, the parent ion cores are inertially confined to the cluster because the much lighter electrons depart quickly, leaving the ion field unscreened. This results in a very large and inhomogeneous electric field; the field at the surface of a cluster of 25 neon atoms when all of the atoms are singly ionized is on the order of 5×10^{12} V/m [9]. This large field lowers the ionization barrier and enables subsequent ionization events to occur, which in turn further increases the field and lowers the ionization barrier. Hence, the fields created by the initial ionization events "ignite" the cluster to undergo further ionization.

To examine our results in light of these two models, all of the probable ionization mechanisms that may be

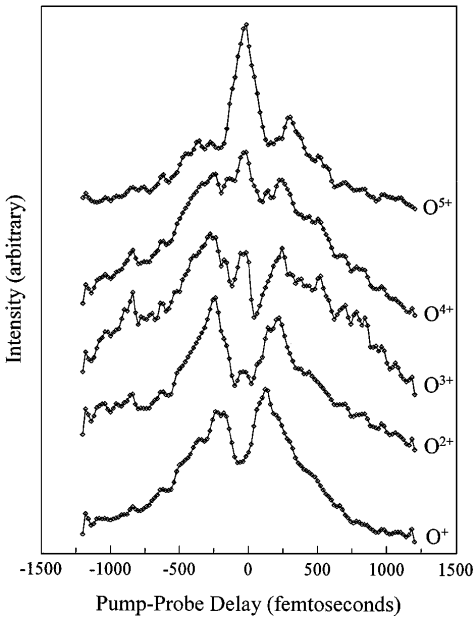

FIG. 3. Pump-probe transients of multicharged oxygen ions, O^{n+} ($1 \leq n \leq 5$), formed through the Coulomb explosion of acetone monomer and acetone clusters.

significant under our conditions must be examined. The first is direct optical ionization, described by the various mechanisms such as barrier suppression ionization [6] and tunneling [6,7] ionization. These mechanisms alone cannot explain the high charge states obtained, but they are important for the initial ionization events.

After the first ions are created within the cluster, additional ionization may occur due to inelastic collisions between the electrons and ions within the cluster, which can be described by the collisional ionization rate formula of Lotz [11]. The rate per ion averaged over a Maxwellian electron distribution is

$$W_{kT} = n_e \frac{a_i q_i}{I_p (kT_e)^{1/2}} \int_{I_p/kT_e}^{\infty} \frac{e^{-x}}{x}\, dx\,, \qquad (1)$$

where n_e is the electron density, I_p is the ionization potential in eV, kT_e is the cluster electron temperature, a_i is an empirical constant (4.5×10^{-14} eV^2/cm^3), and q_i is the number of electrons in the outer shell of the ion. The ionization rate given in Eq. (1) accounts for only the thermal energy of the electrons, not that due to the field of the laser. To estimate the energy of the electrons in the laser field, a rate has been calculated [12] using the collisional ionization cross section of Lotz and treating the electron velocity in the laser field as sinusoidal,

$$W_{\text{laser}}(t) = n_e \sigma_i \frac{eE}{m_e \omega} \sin\omega t\,, \qquad (2)$$

where σ_i is the ionization cross section and E is the laser field in atomic units.

In their CEMM, Rhodes and co-workers have proposed [13] another expression to approximate the number of ionization events:

$$N_x \cong n^{4/3} Z \frac{\sigma_{ei}}{r_0^2} \qquad (n \geq 3)\,, \qquad (3)$$

where n is the number of atoms in the cluster, Z is the resultant ionic charge, σ_{ei} is the inelastic electron impact ionization cross section, and r_0 is the interatomic spacing. Furthermore, the coherent electron motions enhance the number of ionizations given by Eq. (3) because they behave as a quasiparticle of mass Zm_e and charge Ze, requiring modification of the electron impact cross section to the form $\sigma_{ei} \rightarrow Z\sigma_{ei}$.

In the IIM [9], the ionization state obtained is due to the lowering of the barrier to ionization by the nearby ion cores created by the initial ionization events. In contrast to the CEMM, the ion cores in a cluster are responsible for the high charge states obtained, rather than the large electron density. Furthermore, it was concluded that removal of the outer electrons is not expected to be very sensitive to pulse width, cluster size, or atomic weight. A related two atom version of this general model has been proposed by Bandrauk and co-workers [14,15] in their time-dependent quantum mechanical studies of diatomic molecules. They concluded that the rate of ionization is highly dependent upon the internuclear distance, in a nonmonotonic fashion. Additionally, it has been shown [16] that the dependence on internuclear separation is due to the role of electron localization in intense field ionization. Such effects would be expected to give rise to a beating pattern, consistent with present observations.

As the various models predict, we do not observe any multicharged species unless clusters are present in our molecular beam. The charge distributions for the atomic fragment species from the Coulomb explosion of xenon and krypton clusters are well represented by the TOF spectra in Figs. 1 and 2. The charge states obtained are reasonable in considering both the CEMM and the IIM. The charge distributions in Figs. 1 and 2 are not found to be sensitive to the degree of clustering. The cluster distribution was varied by sampling different portions of the molecular beam. The resultant charge distribution was examined from the center of the molecular beam, where the largest clusters are present, to completely off the molecular beam, where only the monomer is present. The multicharged species abruptly appeared in the spectra as medium cluster sizes were obtained. But the charge distribution did not vary with further variation in the cluster distribution as effected by moving the laser to different positions within the beam expansion. The CEMM predicts a strong dependence on the size of the cluster; note the dependence of Eqs. (1) and (2) on the electron density, and Eq. (3) on the number of atoms in the cluster. The IIM predicts very little dependence on the degree of clustering, in agreement with our observations.

It is also observed that, under our ionization conditions, multicharged krypton atoms are observed only when a trace amount of hydrogen iodide is present. In a previous study [2], it was also observed that multicharged argon species are present only with the addition of a small amount of HI. It should be noted that in the case of ionization of HI monomer (IP = 10.39 eV) [17], even with high concentrations in the beam, only singly charged HI and I are observed. It is difficult to understand how the addition of HI would have such a radical effect on the ionization of the krypton clusters in the CEMM. From our observations, neat Kr and Ar clusters are not multiply ionized under our conditions, and HI monomer yields only singly charged species. Therefore, an argon or krypton cluster with a single HI molecule should provide only a single electron in the initial ionization event. The cross section σ_{ei} in Eq. (3) would then be very small and the probability of further ionization would be negligible. However, in the case of ionization ignition, the presence of the single iodine ion core in the krypton cluster may be enough to ignite the cluster by slightly lowering the barrier to ionization in the krypton atoms. Furthermore, we have observed multicharged nitrogen atoms [3] resulting from the Coulomb explosion of neat ammonia clusters. The fact that neat krypton (IP = 14.00 eV) and argon (IP = 15.76 eV) clusters do not exhibit multiple ionization, whereas neat xenon (IP = 12.13 eV), acetone (IP = 9.71 eV), and ammonia

(IP = 10.18 eV) clusters do, suggests that the ability to multiply ionize atoms is insensitive to atomic weight and depends more upon the threshold for single ionization. The role of the ionization potential is evident and in accord with the IIM.

Next, we consider the results of the present study of acetone clusters; the pump-probe transients are seen to display unusual characteristics, namely, asymmetric beating patterns with phase shifts. To account for the beating structure shown in Fig. 3, several possibilities are considered. Could the maxima and minima arise due to laser fluctuations? The maxima and minima do not occur at the same time delays for the different O^{n+} species, and in all of the pump-probe scans, the transients displayed similar structure. Obviously, the observed beating pattern could not arise from the phasing of the pump and probe optical fields since the period of the laser is about 2 fs. Could the structure be evidence of coherent wave-packet motion in the ionized cluster? The power of each pump or probe beam is sufficient to multiply ionize the acetone clusters, and it is unlikely that the cluster can stabilize the large amount of potential energy of multiple positive charges within the cluster. Furthermore, there does not appear to be any periodicity in the transients.

The results of the pump-probe studies provide the following: The pump beam intersects the cluster beam, creating multicharged carbon and oxygen species within the acetone molecules, which are contained within the cluster. As the cluster undergoes electron loss, the probe beam arrives at the cluster at some later time. Depending on the time delay of the probe beam, the interatomic spacings have increased to a particular distance as a result of the nuclear motion arising from the Coulomb explosion process. The structure seen for the transients in Fig. 3 is due to the varying ionization rates as the interatomic spacing is increased, as predicted by Bandrauk [14,15] and Corkum [16]. As the interatomic spacings are varied, the wave function and electron localization is changed, resulting in different ionization rates for the various charge states. This would result in the observed maxima and minima observed in the transients. In this model, the ionization rate is predicted to be a highly irregular function of interatomic distance, in contrast to the CEMM which predicts a monotonic decrease in the degree of ionization with an increase in interatomic distance [see r_0 in Eq. (3)].

Rhodes and co-workers have used the generation of hard x rays from clusters as evidence of inner-shell vacancies, arising from the impact of coherently driven electrons [8,18]. This observation alone cannot be used as evidence for the CEMM; an alternative model has been proposed [19] in which the x-ray generation arises from the hot plasma created in the intense field–rare gas interaction.

In conclusion, we have demonstrated that the high charge states obtained when van der Waals and hydrogen bonded clusters are irradiated with intense laser fields are well described by the IIM [9]. The lack of dependence on the degree of clustering or atomic weight and the strong dependence on ionization potential and interatomic (or intermolecular) distances support this conclusion. Our results cannot totally eliminate the possibility of coherent electron motions, but under our experimental conditions, it is not a major contribution to the multicharging and subsequent Coulomb explosion of clusters. Clearly, however, the IIM warrants refinement via more elaborate classical and quantum mechanical calculations.

Financial support by the U.S. Department of Energy, Grant No. DE-FG02–93ER61602, is gratefully acknowledged.

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