Role of Electron Localization in Intense-Field Molecular Ionization

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The rate of nonlinear ionization is strongly enhanced as a molecule is stretched beyond its equilibrium internuclear separation, reaching a peak rate that is many orders of magnitude greater than that at either small or large distances. The enhancement results from nonadiabatic electron localization near the nuclei and its presence is insensitive to the laser frequency and intensity. Most intense-field dissociative ionization experiments are influenced by this effect.

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Resonant multiphoton ionization is often used in molecular spectroscopy and in the analysis of the outcome of chemical reactions owing to its sensitivity to the electronic structure. As the laser field increases, Stark shifts and broadening of the electronic levels make resonances increasingly less important. We show that at sufficiently high intensities the electronic structure becomes important again. Specifically, the ionization rate of molecules increases dramatically within a characteristic range of internuclear separations, corresponding to the region where the structure of the electronic wave function of the ionizing state changes significantly.

We show, moreover, that the position of the maximum in the ionization rate does not vary significantly between subsequent ionization stages. This result has important implications for the interpretation of a series of experimental studies [1] of strong field molecular ionization. As was suggested by several experiments and conclusively demonstrated in [1(g)], the atomic fragments following dissociative ionization of a variety of molecules possess kinetic energies that constitute a constant fraction of the Coulomb repulsion experienced by the molecular ion at the equilibrium distance. This observation holds for all studied molecules, independent of the charge state and pulse duration [1(g)].

Several models of multielectron dissociative ionization have been proposed. The classical model of Ref. [1(c)] predicts dependence of the ionization on the internuclear separation (R) but implies optimal ionization at different R for different charge states. Thus, the molecule is expected to travel between ionization stages, inconsistent with the observed constant energy ratio [1(g)]. The authors of Ref. [1(e)] interpreted their results for the case of I_2 ionization with 80 fs pulses by suggesting that the heavy molecule is frozen during the pulse duration. It was subsequently demonstrated [1(f)], however, that even for heavy molecules the fragment kinetic energies are essentially independent of the pulse duration in a wide range ($\sim$100 fs–10 ps), thus ruling out the frozen molecule picture. Reference [1(g)] suggests that a certain stabilization mechanism immobilizes the molecules during the interaction. It was pointed out [1(g)], however, that this interpretation is hard to reconcile with the independence of the effect on the intensity.

We suggest that the long-standing experimental puzzle can be accommodated within the more general molecular ionization model described below. We show that intense field molecular ionization differs *qualitatively* from atomic ionization: It depends sensitively on the molecular configuration and hence provides a probe of molecular structure and motions. Although we concentrate on diatomic molecules, our qualitative conclusions extend to larger systems. The sensitivity of the ionization rate to the internuclear separations provides a new mechanism for time-resolving dissociative dynamics using intense laser fields. As will become clear from the discussion below, it is also important for cluster ionization [2], plasma formation [3], charge transfer [4], and dielectric breakdown in femtosecond experiments [5].

Figure 1 shows the Coulomb potential experienced by a valence electron of a diatomic ion in the absence of field [Fig. 1(a)] and in the presence of a constant field [Fig. 1(b)]. At small internuclear distances (dashed curves) the energy of the local maximum is much lower than the energy of the ground electronic state, and ionization is similar to that of an atomic ion, the only difference being the polarizability of molecular ions. At large internuclear distances (dot-dashed curves in Fig. 1) the inner barrier between the two wells is broad and ionization is again atomiclike.

By contrast, at intermediate internuclear separations (solid curves in Fig. 1), the double-well nature of the molecular potential leads to a *qualitative* difference in the ionization dynamics compared with the atomic case. Figure 1(b) suggests that in this region ionization of diatomic ions would be dramatically enhanced compared to atomic ionization since the electron can tunnel through the narrow *internal* barrier directly to the continuum. A similar figure to Fig. 1(b) was included in an early molecular ionization paper [1(c)]. Nevertheless, Thomas-Fermi calculations of molecular ionization [6], performed in the *adiabatic* limit, showed only very modest enhancement in the ionization rate with internuclear separation. In the adiabatic approximation the electronic wave function adjusts as the

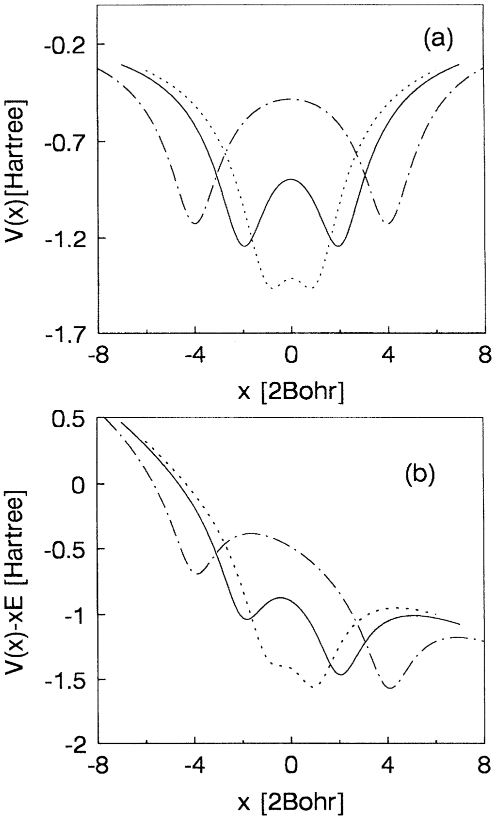

FIG. 1. Schematic illustration of the electronic potential [Eq. (1)] at several internuclear separations in the absence of field (a) and in the presence of a constant field (b): (----) $R = 4$ bohr; (——) $R = 8$ bohr; (· — · — ·—) $R = 14$ bohr.

potential changes during the laser cycle, fully localizing in the lower well in Fig. 1(b), making ionization more difficult.

Nonadiabatic localization of the electronic wave function in the rising well of the potential is a crucial element of our theory. Such localization in strong laser fields is well known to occur in double-well quantum structures (field-induced destruction of tunneling [7]). Tunneling between the wells is suppressed as soon as $RE \gg \omega_{gu}(R)$, where E denotes the electric field strength and $\omega_{gu}(R)$ is the field-free splitting between the ground electronic state of the double-well potential and its asymmetric partner. In this region tunneling is possible only on resonance, $RE \sin \omega t \leq \omega_{gu}(R)$, yielding $\delta t \sim \omega_{gu}(R)/RE\omega$ for the tunneling time per half cycle. A small tunneling exponent $\delta t \omega_{gu}(R) = \omega_{gu}^2(R)/RE\omega < 1$ implies trapping of the population in the rising potential well during the half cycle. As a result, a new ionization mechanism is introduced—tunneling of the trapped population to the *continuum* through the internal barrier [Fig. 1(b)].

The qualitative ionization dynamics suggested by Fig. 1 is supported below by numerical calculations. The calculations show, however, that even qualitatively the ionization dynamics is richer and more complex than that suggested by Fig. 1, particularly for higher charge states. We present also results of an analytical model, applicable at large separations. We consider a generic diatomic ion A_2^{n+} aligned along the electric field vector of the linearly polarized light, with a single active electron moving in a one-dimensional potential

$$V(x,t) = -\frac{Q}{\sqrt{(x-R/2)^2+a^2}} - \frac{Q}{\sqrt{(x+R/2)^2+a^2}} - xEf(t)\sin\omega t\,. \qquad (1)$$

Alignment is typical in strong-field molecular ionization experiments [1]. This has been experimentally verified for both long (few ps) [8] and short (~100 fs) [9] pulses. In addition, typically only laser-aligned ionic fragments are detected [1]. Confining the electron motion to one dimension proved to capture the essential features in studying intense-field atomic ionization [10], and we expect it to be particularly reliable in the aligned diatomic case. In Eq. (1) Q is the nuclear charge and a is a smoothing parameter, routinely employed in strong-field atomic ionization theories [10].

Although this work is intended to explore a *general* effect, rather than to model a specific experiment, in order to make the discussion concrete we adjust the parameters of Eq. (1) to correspond roughly to the intensities, wavelengths, and molecular systems probed in recent experiments [1]. For different values of Q we use $a = 2$, approximating the ionization potential of diatomic ions such at $I_2{}^{n+}$ [1(e),1(f)] or $Cl_2{}^{n+}$ [1(g)] ($n = 2Q - 1$). Our conclusions are sensitive to neither the value of a nor the precise choice of the field parameters, discussed below. The time-dependent Schrödinger equation is solved by exact wave packet propagation, using the split-operator fast Fourier transform method.

Figure 2(a) shows the calculated ionization rate as a function of the internuclear distance for several charge states of the molecular ion. We assume smooth turn-on of the electric field, $f(t) = 1 - \exp(-t/\tau)$ in Eq. (1) with $\tau \approx 20$ fs, and take the initial state to be the ground state of the molecular ion. The ionization rate is computed by following the time decay of the norm. Particular care is taken to ensure that the decay is single exponential by turning the laser field smoothly enough and by propagating the wave packet to sufficiently long times. A complementary picture of the ionization dynamics is given in Fig. 2(b), which shows the total ionization probability following a short pulse, $Ef(t) = E\sin(\pi t/T)$ with $T = 30$ fs. Figures 2(a) and 2(b) correspond to two limiting situations, the former being independent of the experimental details and the latter being independent of a specific decay law.

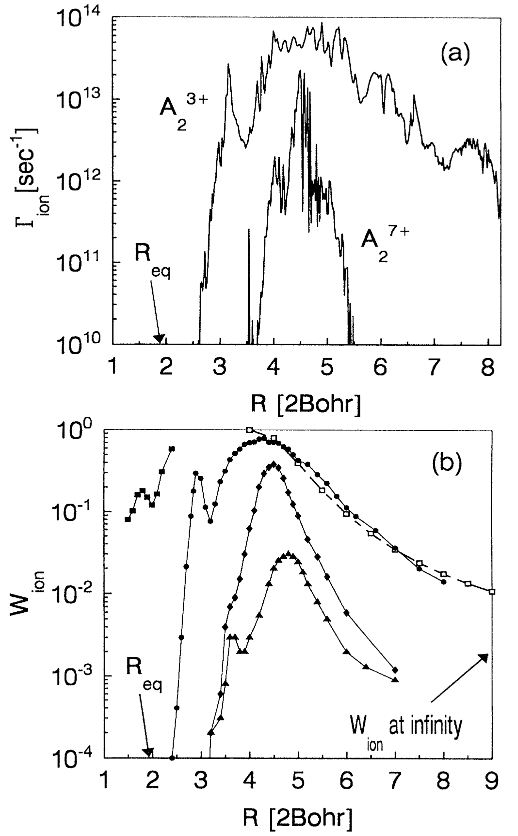

FIG. 2. (a) Ionization rate vs internuclear distance for A_2^{3+} at $I = 9 \times 10^{13}$ W cm^{-2} and A_2^{7+} at $I = 1.2 \times 10^{14}$ W cm^{-2}. The photon energy is 1.1 eV in both cases. (b) Ionization probability following a short pulse, $I(t) = I \sin^2(\pi t/T)$ with $T = 30$ fs. Full squares: numerical probability for A_2^+ at $I = 9 \times 10^{13}$ W cm^{-2}; circles: numerical probability for A_2^{3+} at $I = 9 \times 10^{13}$ W cm^{-2}; open squares: modified ADK model for A_2^{3+} ($R_0 = 2.5$ bohr; see the text for details); triangles: numerical probability for A_2^{5+} at $I = 9 \times 10^{13}$ W cm^{-2}; and diamonds: numerical probability for A_2^{5+} at $I = 1.3 \times 10^{14}$ W cm^{-2}. $\omega = 1.4$ eV in all cases.

There are several important features in Fig. 2: All charge states show strongly enhanced ionization in the same region of internuclear separations. The reason is that electron localization during the laser half cycle occurs at approximately the same R over a range of many charge states. The envelope of the ionization rate is insensitive to the laser frequency in the range we have studied ($0.8 \leq \omega \leq 1.6$ eV). The superimposed resonance structure is sensitive to ω, showing that Fig. 1(b) gives only a simplified picture of the process.

Although the region of R where the ionization rate is maximum shrinks with increasing charge (Fig. 2), the peak value of the ionization rate remains amazingly high while the ionization potential varies from about 25–30 eV (A_2^{3+}) to about 60–70 eV (A_2^{7+}). For the triply charged ion, the ionization rate is almost 3 orders of magnitude greater near its peak than at $R \longrightarrow \infty$. For higher charge states the enhancement is even greater. At $I \approx 9 \times 10^{13}$ W/cm^2 the ionization rate of A_2^{1+} near equilibrium is almost an order of magnitude less than that of A_2^{3+} near the peak. Only a slight increase in intensity to $I \approx 1.3 \times 10^{14}$ W/cm^2 is required to achieve the ionization rate of A_2^{5+} and A_2^{7+} comparable to that of A_2^{1+} near equilibrium (Fig. 2). It would require approximately 1 order of magnitude greater intensity to achieve the same ionization rate for an atomic ion A^{3+}.

The ionization mechanism becomes more complex as one moves to higher charge states (e.g., A_2^{5+}, A_2^{7+}). For large Q in Eq. (1) the ground state in each of the wells of the double-well potential is very deeply bound. At the intensities shown in Fig. 2 the external barrier is not suppressed to below the ground state of the raised well [Fig. 1(b)] until very large R. However, for large Q each well supports more than one localized state even at modest R. These high-lying electronic states have sufficient energy to tunnel to the continuum through the external barrier at the intensities considered. The excitation mechanism of high-lying states is a particular case of resonant tunneling: During the laser half cycle the localized ground state of the rising well [the left well in Fig. 1(b)] passes through resonance with excited states of the descending well, which are thus populated via Landau-Zener transitions. Such excitation occurs also in quantum well devices [11]. Clearly, the excitation is permitted only at internuclear separations where the inner barrier is not too broad. The peak position of the ionization curve is determined by the competition between the excitation process and the tunneling to the continuum. At higher intensities ($I \sim 10^{15}$ W/cm^2) the outer barrier is increasingly suppressed and the resonant tunneling ionization is replaced by tunneling through the inner barrier as described above. The ionization probability increases and its R dependence becomes very similar to that for A_2^{3+} at $I \approx 10^{14}$ W/cm^2.

We now describe a 3D analytical model applicable in the low-frequency–high-intensity limit, which allows calculation of molecular ionization rates at sufficiently large R. With increasing internuclear separation the external barrier becomes irrelevant. In the low-frequency limit ionization can be envisioned as tunneling through the internal barrier, suppressed by the *combined* electric fields of the laser and the adjacent ion. We have applied this point of view to our model triply charged molecular ion and considered tunnel ionization of A^+ in the combined fields of an adjacent doubly charged ion and the laser. The standard (3D) atomic tunneling ionization theory (ADK) [12] was modified by replacing the laser field E by $E_{\mathrm{tot}} = E + E_{\mathrm{ion}} = E + Q/(R - R_0)^2$, where R_0 was chosen to approximately account for the slight offset of the barrier maximum from the nucleus.

The open squares and the full circles in Fig. 2(b) compare the analytical and the numerical ionization probabilities for A_2^{3+}. The two simple models, the 3D quasistatic approximation and the exact solution of the 1D time-dependent Schödinger equation, agree well in the appropriate (large R) limit. As expected, they deviate when R is decreased and the interplay between the two wells starts dominating the ionization dynamics. We note that for H_2^+, R dependence of the ionization rate is implicit in three values ($R = 7$ bohr, 10 bohr, and ∞) of the rate obtained by 3D numerical experiments [13].

Our results suggest that the following scenario takes place in long-pulse multielectron molecular ionization [1]: First, several electrons are stripped until the first repulsive charge state (A_2^{2+} or A_2^{3+}) is reached. The molecule starts to dissociate and enters a critical region $R \approx R_{\mathrm{cr}}$, where the ionization rate is strongly peaked for several successive ionization stages. A simple estimate assuming Coulomb repulsion shows that even as heavy a molecule as I_2^{2+}, starting to dissociate with zero initial kinetic energy at $R_{\mathrm{eq}} \approx 5$ bohr will reach the critical region ($R \approx 9$ bohr) in ca. 110 fs. As seen in Fig. 2(b), the intensity needed to reach the repulsive state A_2^{2+} near equilibrium is sufficient to rapidly ionize several more electrons in the critical region, producing a series of highly charged states. The series is terminated at a state for which the time required for the nuclei to pass the critical region is too short to permit further ionization. Thus, the fragments from all charge states of the molecule have kinetic energies that correspond to Coulomb repulsion at approximately the same internuclear distance R_{cr}. These energies constitute a constant fraction $R_{\mathrm{eq}}/R_{\mathrm{cr}}$ of the Coulomb energy at the equilibrium distance, independent of the charge state and pulse duration. This answers the experimental puzzle discussed in Ref. [1(g)].

One can estimate R_{cr} by approximately calculating the distance where the internal barrier penetrates the ground state and the interplay between the two barriers starts to dominate ionization dynamics. Using the approximation that the ionization potential of an atomic ion with charge $Q - 1$ is QI_p, where I_p is the atomic ionization potential, we find that localization occurs at $R_{\mathrm{cr}} \sim 3/I_p$, independent of Q. One obtains $R_{\mathrm{cr}} = 2.87$ (2.34), 3.1 (2.62), 3.1 (2.75), 3.3 (2.8), and 3.9 (3.6) Å for N_2, O_2, H_2, Cl_2, and I_2, respectively. This slightly and consistently overestimates the distances (shown in parentheses) suggested by experimental explosion energies [1(g)] and agrees well with the numerically computed onset of enhancement in Fig. 2.

The key feature in molecular ionization is the multiple-well structure of the ionic potential and the electron localization that it implies. We have extended the linear model to triatomic molecular ions as a first step to confirm the generality of the results. As for diatomics, we find strong enhancement of the ionization rate of triatomic ions as either or both bonds are stretched to a critical region. The sensitivity of the ionization rate to the internuclear separations suggests the possibility of using intense-field ionization as a universal probe in time-resolved pump-probe spectroscopy, e.g., to observe dissociative motion. Because of space limitations we defer detailed discussion of the results to a later paper.

Our results have important implications also to several other fields. An ion in close proximity with an atom, a molecule, or another ion is found in many areas of physics. These include cluster ionization [2], plasma formation [3], and dielectric breakdown [5], to mention but a few. Enhanced ionization, which is sensitive to the nuclear coordinates, is likely to play a role in all these situations.

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Note added.—We would like to call the reader's attention to a paper by Zuo and Bandrauk [14] where enhanced ionization of H_2^+ is extensively studied using a fully three-dimensional model.

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