

Coulomb Explosion of Large Polyatomic Molecules Assisted by Nonadiabatic Charge Localization

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The electron-nuclear dynamics of the Coulomb explosion of a large polyatomic molecule, anthracene, is probed using kinetic energy distributions of produced H^+ ions. The kinetic energy release of ejected protons exceeds 30 eV for anthracene exposed to 10^{14} W cm^{-2} , 800 nm pulses of 60 fs duration. We propose a strong-field charge localization model, based on nonadiabatic dynamics of charge distribution in a (multiply) ionized molecule; the charge localization lasts many laser periods and is sustained through successive ionizations of the molecular ion. The model explains quantitatively the dependence of the H^+ kinetic energy on the laser intensity. Dissociative ionization of a polyatomic molecule enabled by long-lived charge localization is a new type of electron-nuclear dynamics and is essential for understanding the pathways of molecular or ionic fragmentation in strong fields.

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Understanding the electronic and nuclear dynamics of polyatomic molecules exposed to intense ultrafast laser pulses is central for controlling [1] and creating new [2] laser-induced chemical reaction pathways. The measurement of the kinetic energy distributions of the ejected H^+ is an important new tool for probing the dynamics of organic molecules in the strong-field excitation regime. Highly energetic dissociation of a molecule resulting from multiple ionization, known as the ‘‘Coulomb explosion’’ [3], has been the subject of numerous investigations covering both diatomic [4,5] and polyatomic [6,7] molecules. At ultrahigh laser intensities ($I \geq 10^{16}$ W cm^{-2}) the electron ponderomotive energy [8], $U_p = e^2 E_0^2 / (4m_e \omega^2)$, significantly exceeds the characteristic energy level spacing of a molecule, Δ . [Here $E_0 = \sqrt{2I}/(\epsilon_0 c)$ and ω are the laser field amplitude and frequency, respectively, m_e is electron mass, ϵ_0 is vacuum permittivity, and e is the fundamental charge.] In the $U_p \gg \Delta$ laser intensity regime the electron-nuclear dynamics of the Coulomb explosion has been explained by microplasma [9,10] or hydrodynamic [11] models. These models do not address the complex dynamics of electronic excitations occurring at lower laser intensities, in the $U_p \sim \Delta$ regime, where the outcome of laser-molecule coupling is inherently sensitive to the details of the molecular Hamiltonian. In this regime, the interplay of electronic excitations and dissociation in diatomic molecules has been described by the charge-resonance-enhanced ionization model [12,13]. None of the existing models address dissociative ionization of polyatomic molecules in this $U_p \sim \Delta$ regime, which is most interesting from the control viewpoint. Thus, it is of considerable interest to study experimentally and understand theoretically strong-field photodissociation of polyatomic molecules in this setting.

The kinetic energy release of H^+ formed in the Coulomb explosion of anthracene, $C_{14}H_{10}$ (see Fig. 1), after near-IR laser pulse excitation is measured as a function of laser intensity. Anthracene is chosen because the conclusions drawn from studying this molecule can be generalized to many other polyatomic molecules. To explain the dependence of the measured H^+ energy distributions on I , we propose a model in which the dynamic polarization of dissociating polyatomic ions results in

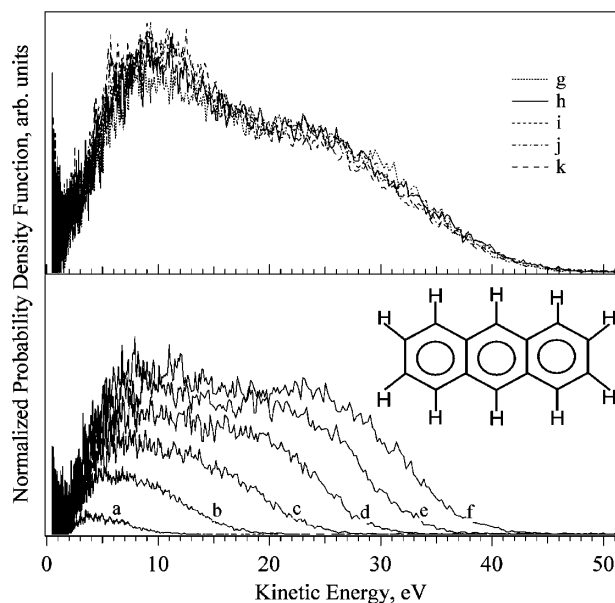


FIG. 1. Kinetic energy distributions of H^+ at increasing laser intensities ($\times 10^{14}$ W cm^{-2}): (a) 0.49; (b) 0.66; (c) 0.89; (d) 1.2; (e) 1.6; (f) 2.2; (g) 2.96; (h) 3.19; (i) 3.44; (j) 3.71; (k) 4.00. The upper panel illustrates the saturation of the kinetic energy release at higher laser intensities.

charge localization lasting for many laser cycles, and sustained through successive ionizations. This charge localization results in an increase of local Coulomb repulsion in a large ion and is a new type of electron-nuclear dynamics, characteristic of large polyatomic systems. The mechanism of such photodissociation assisted by sustained charge localization is qualitatively different from the Coulomb explosion of diatomic molecules.

Ions were collected using a linear 1 m time-of-flight (TOF) mass spectrometer. A 1 mm aperture was placed between the ionization and detection regions of the spectrometer to restrict the signal collection to the near-focal cylindrical volume of the laser beam [14]. A regeneratively amplified Ti:sapphire laser produced 10 Hz, 1.5 mJ, 60 fs pulses centered at 800 nm. The intensities were calibrated by comparison to the appearance thresholds for multiply charged argon. Solid sample sublimed directly into vacuum to attain pressure of $\sim 1 \times 10^{-6}$ Torr (the space-charge effects were insignificant at such a low pressure); the background pressure for the spectrometer was $\sim 1 \times 10^{-8}$ Torr.

The kinetic energy of H^+ was measured in two complementary experiments [15]. In the first, ions were allowed to drift ~ 5 mm in field-free conditions (prior to being extracted into the mass spectrometer by a +500 V potential), separating according to their initial velocities during the drift period. In the second experiment, the ions were exposed to a retarding field before extraction into the TOF system. This allows calibration of the TOF distributions in terms of kinetic energy. Using the zero-field ion collection mode we obtained TOF spectra for H^+ , and converted the measurements into kinetic energy distributions using the calibrating retarding field measurements and Jacobian intensity transformations.

Figure 1 shows the kinetic energy distributions of H^+ at increasing laser intensities. To quantitatively characterize the distributions we use the dependence of maximum (cutoff) energy, E_{\max} , on I , shown in Fig. 2. The kinetic energy distributions exhibit nontrivial dependence on I . At lower I (from 4.0 to 9.0×10^{13} $W\text{ cm}^{-2}$) the distribu-

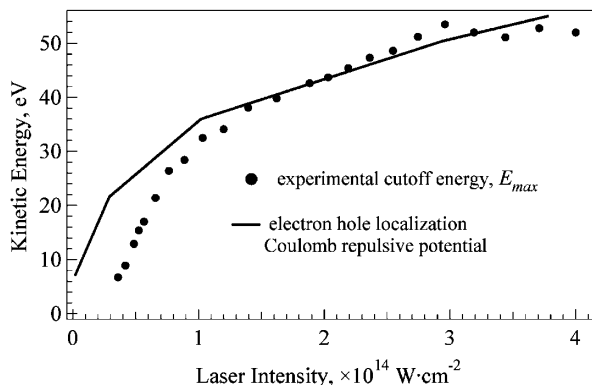


FIG. 2. The cutoff values of the H^+ kinetic energy distributions and model maximum Coulomb potential expelling H^+ , as a function of I .

tions are broad and featureless [Figs. 1(a)–1(c)]. Both the most probable kinetic energy value and E_{\max} increase linearly with I . However, as the laser intensity approaches $\sim 1 \times 10^{14}$ $W\text{ cm}^{-2}$, this simple trend changes qualitatively. At 1.1×10^{14} $W\text{ cm}^{-2}$ the distributions become distinctly bimodal. The most probable values of the low-energy and the high-energy features increase with I from 8 ± 1 eV and 15 ± 1 eV at 1.1×10^{14} $W\text{ cm}^{-2}$ to 10 ± 1 eV and 25 ± 2 eV at 4.0×10^{14} $W\text{ cm}^{-2}$, respectively. Notably, in this laser intensity range the $E_{\max}(I)$ dependence becomes sublinear; the cutoff energy saturates at 50 ± 2 eV.

To understand the rapid initial growth and eventual saturation of the H^+ kinetic energy release with increasing I , we consider the dynamics of both ionization and polarization of anthracene by these intense laser pulses. A trivial explanation for the growth of the H^+ kinetic energy with I is the Coulomb explosion process, in which the degree of ionization of the parent ion, Z , increases with I , thereby increasing the repulsive potential, U_{H^+} . Is this sufficient to account for the growth of E_{\max} from 8 to 30 eV as I increases from 0.4 to 1.0×10^{14} $W\text{ cm}^{-2}$? The kinetic energy acquired by H^+ due to repulsion from the electric charge $(Z-1)e$ distributed over the parent polyatomic ion can be estimated as $E_Z(\text{eV}) = 14.4(Z-1)/R_{ZH}(\text{\AA})$. Here, $1/R_{ZH}$ is the average of the inverse distances from the proton to the ion's nuclei; for anthracene, we estimate R_{ZH} to be ~ 3.5 \AA . In this case, the formation of H^+ with kinetic energies of 8 and 30 eV requires ionization stages of $Z = 3$ and 9, respectively. This method underestimates the necessary degree of ionization, especially for large values of Z (a proton begins accelerating as soon as ionization starts, before the estimated value of Z is achieved, thus exposing H^+ to a reduced U_{H^+}).

Are these degrees of ionization of anthracene realistic at the relevant laser intensities? Our quantitative theory of nonadiabatic excitation of polyatomic molecules and ions in strong laser fields [16] predicts saturation of double ionization of anthracene at $I \sim 4 \times 10^{13}$ $W\text{ cm}^{-2}$; therefore, we expect triple ionization to start at this I . Thus, the observed kinetic energies of H^+ ranging from 5 to 8 eV may result from the formation of $Z = 3$ molecular ions. However, it is hard to justify the jump in the degree of ionization from $Z = 3$ to $Z > 9$ as I increases modestly (by a factor of 2.5) from 0.4 to 1.0×10^{14} $W\text{ cm}^{-2}$. Currently, no theory or available data indicate that Z should increase dramatically in this small window of laser intensities.

What other factors could enhance the observed H^+ kinetic energy? When an ensemble of molecules is considered, thermal fluctuations induce a variance in R_{ZH} , widening the kinetic energy distributions. The increase in energy is caused by (i) electron density fluctuations and (ii) vibrational bond-length fluctuations. The first factor depends exponentially on the ratio of interlevel energy spacing (≥ 1 eV) to the thermal energy (0.025 eV) and, thus, is negligibly small. The second factor gives the

interatomic length variation $\leq 0.1 \text{ \AA}$ for both C-C and C-H vibrations in polyaromatics, resulting in energy spread of $< 0.5 \text{ eV}$. Other ensemble averaging factors, such as angular distribution, can decrease only the kinetic energy release (this is why we refer to these calculated values as cutoff energies). Because the known peak-broadening mechanisms cannot explain the observed H^+ energies within the framework of the Coulomb explosion model, we need to address the dynamics of charge redistribution in a polyatomic ion. The U_{H^+} is significantly modified by the strong oscillating electric field inducing time-dependent polarization of the molecule and its multiply charged ions. For a diatomic, polarization can decrease only U_{H^+} in comparison with the symmetric charge distribution. Contrary to this, large ions can develop much stronger *local* Coulomb repulsion. Provided the nearest end of the ion is positively polarized during the proton acceleration, the expelled H^+ will acquire additional energy.

A charge localization model, based on electron hole motion, can capture the essence of the observed $E_{\max}(I)$ dependence and provide an insight into the cause of the H^+ energy saturation. To model the charge distribution in strongly polarized ions of various charge states Z , we assume that the electric field is strong enough to concentrate all of the positive charge (the “electron holes” resulting from ionization) at one of the terminal aromatic rings, thus moving $\sim Z/2$ holes across the molecule. (We estimate that in such a strongly polarized anthracene ion, the average inverse distance between the effective charge and the expelled H^+ , R_{ZH} , is $\sim 2 \text{ \AA}$.) In this case, the polarization energy, P , can be estimated as $P = f(N)e^2/R - eN\epsilon L$, where N is the number of the transferred electron holes. The first term is because of an increase in Coulomb repulsion ($R \sim 1.5 \text{ \AA}$ is the radius of the aromatic ring); the second term is due to transfer of N charges over the distance $L \approx 4R$ by the electric field ϵ . Because Coulomb repulsion is proportional to the square of the localized charge density, $f(N)$ is a steep function, asymptotically quadratic in N . Setting $P = 0$, we estimate the upper limit on the number of localized charges, $2N$, as a function of I . Using the $N(I)$ dependence we calculate the maximum Coulomb potential expelling the protons as $U_{H^+}(I) = 14.4(2N - 1)/R_{ZH}(\text{\AA})$, shown as a solid line in Fig. 2. The measured values of E_{\max} are smaller than U_{H^+} for $I < 10^{13} \text{ W cm}^{-2}$ and approach the model case at $I > 10^{14} \text{ W cm}^{-2}$.

This difference at $I < 10^{14} \text{ W cm}^{-2}$ arises because the model overestimates P in the regime $U_p < \Delta$. In the low-intensity regime, two effects can reduce the acting repulsive potential. First, at low I , the actual degree of ionization Z is smaller than $2N$, thus making the real U_{H^+} smaller than predicted by the model. As I increases, multiple ionization provides the necessary number of charges to be localized, and the agreement between the model and the measurement improves. Second, the remaining electrons screen the outgoing proton from

the positive charge, effectively reducing U_{H^+} . We qualitatively approximate the screening effect by an exponential factor, $\exp\{-R_{ZH}/a[Z(I)]\}$. Here, the characteristic screening length a depends on the ionization degree Z , i.e., on the laser intensity I . The use of an intensity-dependent screening length can capture the low-intensity response of the experimental cutoff behavior within experimental error. Forgoing *ab initio* calculations of the screening length, we expect a to increase with decreasing laser intensity, because more valence electrons remain bound at lower I . The dependence $a(I)$ may give an initial insight toward calculating a realistic screening in a finite molecular system (a separate formidable problem).

In the gas-phase ensemble, the anthracene ions are randomly oriented and are too large to be forced into alignment during the 60 fs laser pulses. The localized charge distribution occurs in the ions oriented along the field polarization vector; in ions of transverse orientation the delocalized distribution is expected. This correlates well with the two distinct features observed in the H^+ energy distributions. We attribute the high-energy feature to the charge localization phenomenon, and explain the low-energy feature by simple Coulomb explosion.

How long should the charge localization last to explain the observed H^+ kinetic energy? If polarization of an ion followed the oscillating field adiabatically, the local charge at the ion's ends would exceed significantly its average value during $\sim \frac{1}{4}$ of the laser cycle (i.e., about 0.65 fs for the 800 nm laser). If the proton acceleration time is greater, the localized charge effect will substantially decrease. For an acceleration time exceeding the charge oscillation period, the final kinetic energy will rather reflect the time-averaged potential U_{H^+} . The ponderomotive contribution of the fast-oscillating component is as small as $(1/4m\omega^2)(dU_{H^+}/dr)^2 \ll 1 \text{ eV}$. Thus, polarization of an ion will significantly increase H^+ kinetic energy only if it lasts for time periods much longer than $\pi/2\omega$.

To estimate the necessary duration of charge localization, we calculated the time for an H^+ to be accelerated to a given kinetic energy from a strongly polarized molecular ion. While an infinitely long acceleration converts all of the Coulomb energy $E_Z(\text{eV})$ to kinetic energy, acceleration during a finite time, t_Z , results in kinetic energy $E(t) < E_Z$. The time t_Z , expressed as a function of a dimensionless parameter $\chi = E(t)/E_Z$, is $t_Z = \tau_Z[\sqrt{\chi}/(1 - \chi) + \ln(1 + \sqrt{\chi}) - 0.5 \ln(1 - \chi)]$. Here τ_Z is the characteristic acceleration time given by $\tau_Z = \sqrt{2\pi\epsilon_0 m_p R_{ZH}^3/[e^2(Z - 1)]}$; m_p is proton mass. The values of t_Z for H^+ expelled from strongly polarized molecular ions of realistic charge states Z ranging from 4 to 6, are plotted in Fig. 3 as a function of $E(t)$. Clearly, to contribute substantially to the final H^+ kinetic energy, the polarized charge must be nonadiabatically localized at the same end of the ion for many laser cycles.

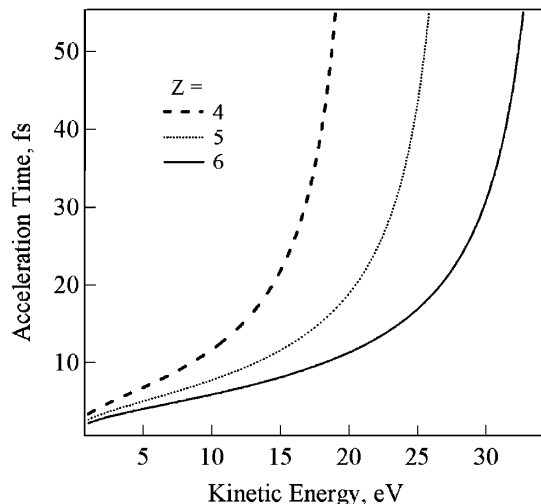


FIG. 3. Acceleration time of H^+ due to electrostatic repulsion from strongly polarized ions of various charge states Z for the initial charge separation $R_{ZH} = 2.0 \text{ \AA}$.

The phenomenon of nonadiabatic localization was considered theoretically in two limiting cases: the double-well [12,13,17,18] and the infinite periodic potentials [19]. In polyatomic molecules, the physical origin of the sustained nonadiabatic electron localization can be traced back to the nonresonant electronic excitation [16]. Initially, a strong laser field causes a Landau-Dykhne [20] electronic transition to the lowest charge-transfer state (one of the two degenerate states with asymmetric charge distribution). This doorway excitation is followed by rapid energy absorption leading to ionization. The molecular ion, formed in its ground state, also undergoes nonadiabatic excitation, resulting in second ionization [16]. Several successive excitation-ionization stages occur during H^+ acceleration, each stage requiring an electronic transition to one of the pair of ionic charge-transfer states. If these two states were degenerate, the transition would occur indiscriminately to either state, and the accelerated H^+ would experience attractive and repulsive forces, resulting in a negligible increase of the H^+ kinetic energy. However, the molecular symmetry is broken [21] by asymmetric nuclear motion (particularly the motion of the accelerated proton itself). As a result, the charge-transfer state degeneracy is lifted, and the ongoing dissociation at the more positive end of the successive ions further increases the gap between the ionic charge-transfer states. Hence, charge localization at the same end of the ion is sustained through successive ionizations.

In conclusion, we observed two distinct regimes of H^+ ejection dynamics. At lower laser intensities, the H^+ kinetic energy increases rapidly with I . At higher I , the kinetic energy release saturates. To acquire the measured energies the outgoing H^+ must be exposed to large electric charge for time periods much longer than the laser cycle. The exposure is achieved by nonadiabatic localization of electrons maintained through successive

ionizations during H^+ expulsion. A model based on non-adiabatic dynamics of electron holes captures the essence of the measured H^+ kinetic energy dependence on I . In this model the dissociative ionization of polyatomic molecules is assisted by prolonged nonadiabatic charge localization. In contrast to the Coulomb explosion of small molecules (where the processes of ionization and dissociation can be understood independently), in this model the electron and nuclear dynamics are strongly coupled. The processes of strong-field electronic excitation, ionization, and dissociation cannot be adequately understood as a sequence of independent events in which dissociation is a mere consequence of multiple ionization. The proposed coupled strong-field electron-nuclear dynamics is conceptually important for a host of processes occurring with polyatomic molecules in strong laser fields; its understanding will open new prospects for effective quantum control of strong-field molecular fragmentation and reactivity.

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