Nonadiabatic Multielectron Dynamics in Strong Field Molecular Ionization

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We report the observation of a general strong field ionization mechanism due to highly nonadiabatic multielectron excitation dynamics in polyatomic molecules. We observe that such excitation mechanisms greatly affect molecular ionization, fragmentation, and energetics. We characterized this phenomenon as a function of optical frequency, intensity, and molecular properties.

A revolutionary aspect of modern laser science is the ability to apply electric forces which exceed those that bind matter. Femtosecond lasers allow this to be done with high precision and little energy. This has led to important highly nonlinear processes such as ultrahigh harmonic generation [1], x-ray generation [2], production of highly charged fast particles [3] and neutrons [4] in optically triggered explosions of clusters [5], Coulomb explosions of molecules [6], and strong field control of chemical processes [7]. For very short pulse durations, the molecular response in the strong field is dominated by the electrons and is the subject of this Letter.

The small dimension of atoms means that the electronic motion is faster than the time scale of typical (visible or near infrared) laser field oscillations, leading to an adiabatic (quasistatic) picture of electronic dynamics. The instantaneous laser field suppresses the core potential, allowing the active electron to tunnel out or, in still stronger fields, to escape over the barrier. Optical tunneling occurs when the Keldysh parameter $\gamma = \omega_L \tau_t$ is less than unity. Here ω_L is the laser frequency and τ_t is the atomic tunneling time: $\tau_t = \sqrt{2I_p}/\mathcal{E}$ where I_p is the ionization potential and $\mathcal{E}$ is the laser field strength (atomic units). The strong field ionization of molecules has also largely been modeled within this quasistatic picture, with corrections [8,9] to account for the extended molecular geometry and polarizability, including modification of the Keldysh parameter [8]. However, in polyatomic molecules with many delocalized electrons neither the single active electron nor quasistatic perspectives may remain reliable, even in low-frequency fields. First, the electronic motions in delocalized molecular orbitals are typically much slower than those in atoms and may not adiabatically follow the laser field. Second, in most molecules, multielectron excitations typically lie below the first ionization potential and the inner valence electrons move with frequencies comparable to the outer valence electrons, rendering a single active electron picture inadequate.

We report our studies of polyatomic molecular excitation ionization and fragmentation as a function of laser intensity, wavelength, and molecular size in strong nonresonant laser fields. Using unsaturated linear hydrocarbons with similar electronic structure but different lengths L, *hexatriene* (7.2 Å), *all trans-decatetraene* (13.5 Å) and β-*carotene* (32 Å), and by continuously tuning the laser wavelength between 1.5 and 0.8 μm, we observe and systematically study the transition from quasistatic tunneling behavior to a new excitation-ionization mechanism based on nonadiabatic multielectron (NME) dynamics.

Mechanisms of multielectron ionization such as the enhanced ionization of small molecules [10] and its cluster counterpart, ionization ignition [11], require electron localization at the nuclei. In molecules, they apply at longer times when nuclear motion sets in and leads to the creation of highly charged states during the fragmentation process. By contrast, here we are interested in the dynamics of delocalized electrons in nonstatic fields and therefore used short 40 fs pulses to limit fragmentation-induced electron localization. We avoided strong multiple ionization and subsequent Coulomb explosion [3,5,6] by staying within the $I \sim 10^{13}$–10^{14} W/cm^2 range.

The experimental details are reported elsewhere [12]. In brief, we used tunable 0.8–1.5 μm and 0.4 μm 40 femtosecond pulses. Molecules were introduced via a seeded molecular beam into a small aperture (0.3 mm) time-of-flight mass spectrometer. The laser polarization was aligned along the time-of-flight axis. Absolute intensities were determined, at all frequencies, using the well-studied ionization of atomic Xe as a reference standard. Translational energy distributions for 70 fs, 0.7 μm ionization fragmentation of *all trans-decatetraene* were recorded in a large aperture mass spectrometer [13].

In Fig. 1, we show mass spectra for strong field ionization of these three molecules at two of the wavelengths studied. For hexatriene (HT), the mass spectra obtained at $I \sim 10^{14}$ W/cm^2 at 0.8 and 1.45 μm are very similar. Both show large peaks due to singly and doubly charged parent ions, with little or no fragmentation. This wavelength-independent pattern, which is expected for quasistatic tunnel ionization [14] and adiabatic electronic dynamics, is shown by HT over the whole range $0.8 < \lambda < 1.6$ μm.

At $I \sim 10^{14}$ W/cm^2 and $\lambda = 1.45$ μm decatetraene (DT) also yields mass spectra which are characteristic of
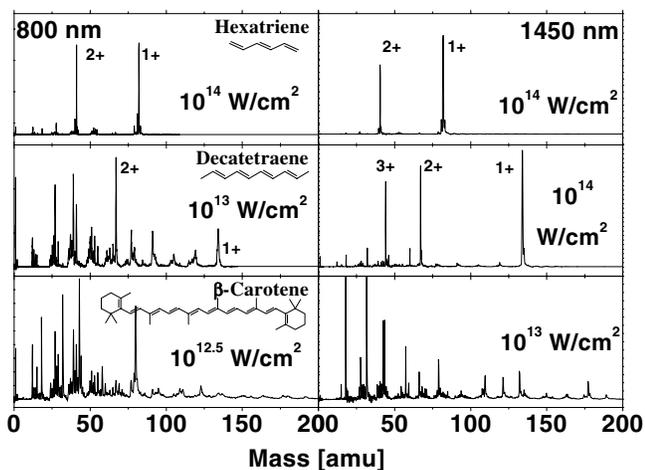
FIG. 1.   Mass spectra of linear, fully conjugated all trans hydrocarbons of increasing length: hexatriene, decatetraene, and β-carotene, using broadly tunable, intense 40 fs pulses, shown at characteristic wavelengths of 800 and 1450 nm. Hexatriene (7.2 Å) shows little fragmentation of several charge states of the parent molecule, a characteristic of tunnel ionization. Longer decatetraene (13.5 Å) shows a similar result at 1450 nm but its fragmentation patterns vary with wavelength, exhibiting a transition to very extensive fragmentation by 800 nm. Much longer β-carotene (35 Å) shows extensive fragmentation at all wavelengths studied. Absolute intensities were determined using atomic Xe as a reference standard.

quasistatic tunnel ionization [14]: stable singly, doubly, and triply charged parent ions with little fragmentation. By contrast, at 0.8 μm DT fragments very strongly at the much lower laser intensity of $I \sim 10^{13}$ W/cm^2. The wavelength dependence of the DT mass spectra demonstrates that the ionization dynamics cannot be adiabatic (wavelength independent) and the quasistatic tunneling picture simply fails. Importantly, this difference cannot, due to the large ac Stark shifts involved (~ 10 eV), originate from optical resonances, as discussed below. Furthermore, the triply charged parent ion is stable and therefore the extensive fragmentation observed at 0.8 μm is due to electronically excited ion states which dissociate after the 40 fs laser pulse is over. This hints that a multi-electron excitation-ionization mechanism is involved.

For all intensities and wavelengths between 0.4 and 1.5 μm, β-carotene is completely fragmented, suggestive of an ionization process similar to that in DT at 0.8 μm and very different from that in DT at 1.45 μm and HT at all wavelengths. In summary, the results of Fig. 1 clearly demonstrate the onset of a nonadiabatic excitation-ionization mechanism and that the failure of the quasistatic tunneling model of molecular ionization depends on molecular properties such as length.

We consider two possibilities for the large energy absorption leading to the extensive fragmentation seen in Fig. 1. One is that a single active electron experiences extensive above-threshold absorption, reaching a superexcited state of the ion which undergoes decay and fragmen-

tation after the laser pulse is over. The other possibility is that many active electrons are absorbing energy from the laser field to form multiply excited states of the ion core. In Fig. 2, we show fragmentation patterns in decatetraene for 70 fs, 0.7 μm ionization at intensities of $I \sim 10^{12}$ W/cm^2 and $I \sim 10^{13}$ W/cm^2. It can be seen that even at the lowest intensities where the signal can be observed, $I \sim 10^{12}$ W/cm^2 (Fig. 2a, 1 count per 200–300 laser shots), the fragmentation is as severe as at $I \sim 10^{13}$ W/cm^2 (Fig. 2b) where the signal is much larger. These results cannot be reconciled with the single active electron above-threshold absorption, which is a highly nonlinear function of intensity and would yield much less fragmentation at lower intensity.

At $I \sim 10^{13}$ W/cm^2 kinetic energy release in the fragments is beyond that expected for simple photochemical bond cleavage in polyatomic molecules. The inset of Fig. 2b shows that the 12–15 amu (CH$_x$, $x = 1$–3) peaks yield an average kinetic energy release of 1.25 eV. Furthermore, the double peak structure shows that the dissociation is highly directional, in contradiction with simple bond rupture unimolecular decay [15] where isotropic emission is expected. We note that the large aperture mass spectrometer used in this measurement did not vignette the ion trajectories. Since the molecules are initially randomly oriented and alignment during the short pulse is not possible, the excitation and ionization dynamics must be strongly sensitive to the alignment of the long molecular axis with respect to the laser field. This explains the directionality of the photofragment emission.

Analyses of the peak shapes for the C_2^+ and C_3^+ fragments indicate average (maximal) kinetic energies of 2 eV (4.2 eV) and 0.9 eV (3 eV), respectively. While these kinetic energies are well below those typically observed in intense-field Coulomb explosion of multiply charged molecular ions [5,6], they are much higher than those
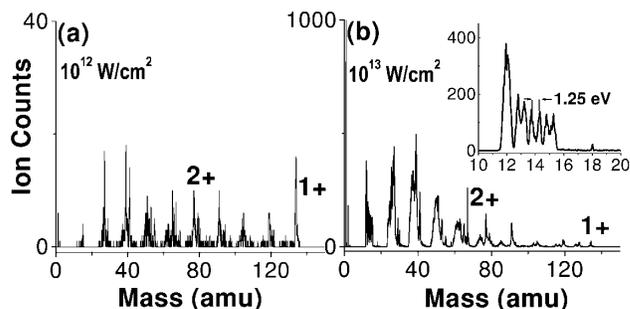

FIG. 2.   Mass spectra of all trans-decatetraene at different laser intensities, using 700 nm, 70 fs pulses. Even at the threshold intensity for detection (1 ion per 250 laser shots), extensive fragmentation is observed. At higher intensities, the signal shows significant kinetic energy release in the fragments. Inset: the methyl group part of the mass spectrum (12–15 amu). The forward-backward splitting corresponds to CH$_3$ fragment average energies of 1.25 eV and highly directional emission, uncharacteristic of typical unimolecular decomposition in photoexcited ions.

expected for typical unimolecular decomposition of excited ions [16]. C-C sigma bond fission processes observed here are typically slow compared to our 40 fs laser pulse duration. These results suggest that multielectron excitation leads to a highly excited parent ion which subsequently fragments, assisted by Coulomb repulsion.

In order to study the transition to NME dynamics, we show in Fig. 3b the wavelength dependence of ionization and fragmentation in DT by plotting the saturation intensity $I_{sat}(\lambda)$. I_{sat} is defined as the onset of 100% efficiency ionization for a given molecule. In Fig. 3a, by using the semilog plot of ion signal S versus $\log(I)$, I_{sat} is determined by extrapolation to zero of the linear part of S [17]. For adiabatic electron dynamics and tunnel ionization I_{sat} would be independent (at constant intensity) of the laser wavelength. As seen in Fig. 3b, the wavelength-independent behavior of $I_{sat}(\lambda)$ is reached around 1.45 μm, fully consistent with the change in fragmentation patterns seen in Fig. 1b. Between 1.45 and 0.8 μm I_{sat} decreases by a factor of 4–5, implying a dramatic increase in the (highly nonlinear) ionization rate towards 0.8 μm. This transition from quasistatic behavior to a dynamic absorption cannot be interpreted as a consequence of resonant photon absorption, as would seem natural in the perturbative limit. Indeed, at these intensities, the voltage $\mathcal{E}L$ applied by the laser field across the molecule approaches a typical ionization potential $I_p \sim 10$ eV, meaning that the ac Stark shifts of *delocalized* molecular orbitals approach I_p and the discrete level structure that governs energy absorption in weak laser fields becomes irrelevant.
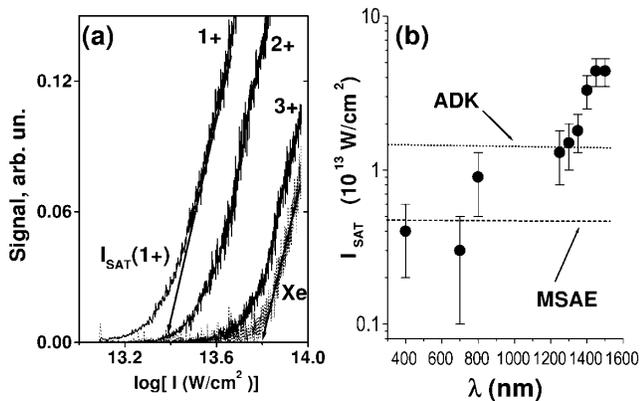

FIG. 3. The wavelength dependence of the saturation intensity I_{sat} for all trans-decatetraene shows dramatic deviation from both atomic tunnel ionization behavior (dotted line) and molecular single active electron pictures (dashed line). (a) The determination of I_{sat} at each wavelength is via extrapolation of the linear part of the ion yield vs log (laser intensity) plot, here shown for 1500 nm. For details, see the text. Absolute intensities were determined using Xe as a reference standard. (b) I_{sat} increases by ~400% between 800 and 1500 nm, significantly exceeding the atomic tunneling limit (ADK) and the molecular single active electron model (MSAE) by $\lambda \sim 1.4$ μm.

Figure 3 not only shows the onset of NME dynamics, but also demonstrates the importance of multielectron effects in the long-wavelength limit. Using the ionization potential appropriate to DT, we show in Fig. 3b the atomic tunnel ionization result (dotted line) and the prediction of the molecular single active electron (MSAE) tunneling model [8], with ionization potential and length of DT (dashed line). The MSAE model corrects the atomic result by accounting for the change in the tunneling barrier due to the molecular length [8]. The experimental long-wavelength limit I_{sat} is significantly above both of these single active electron models. The multielectron effect originates in the dynamic polarization of all delocalized electrons in the strong field which, via Coulomb interactions, repel the "active" electron, thereby effectively increasing the barrier for tunneling.

In summary, Figs. 1–3 show that as the length of a molecular delocalized electron path increases, the excitation/ionization dynamics changes from quasistatic tunneling to NME dynamics, leading to large energy absorption even at threshold intensities, inconsistent with standard above-threshold absorption. Importantly, the departure from quasistatic tunneling can occur even when the Keldysh parameter γ is less than unity, whether corrected or not for molecular size effects [8] (see Fig. 3). For DT, the departure starts at $\gamma^2 \sim 0.06$ (without molecular size corrections that further reduce its value), formally well into the tunneling regime.

The Keldysh parameter relates only to the tunneling motion under the potential barrier and ignores electronic dynamics *inside* the molecule. Qualitatively, the amplitude of electron oscillation $a_{osc} = \mathcal{E}/\omega_L^2$ must be compared to L—the length of a delocalized electron path inside the molecule. There are two cases, $a_{osc} \gg L$ and $a_{osc} \ll L$. Classically, when $a_{osc} \gg L$ the electron is scattered off the edges of the potential well twice every laser cycle. The typical energy absorbed during this event is $E_{scat} \sim \mathcal{E}L$. In the other limit of $a_{osc} \ll L$, $E_{scat} \sim U_p = \mathcal{E}^2/4\omega_L^2$—the average energy of electron oscillation in the laser field. When $I_p < U_p$, the atomic Keldysh parameter $\gamma = \sqrt{I_p/2U_p}$ is less than unity, usually interpreted as tunneling. However, $a_{osc} \ll L$ and therefore ionization can proceed rather via absorption of energy $\sim U_p$ in one scattering event, followed by over-the-barrier escape during the next laser cycle. This is in contradiction with a tunneling picture and the discrepancy stems from $a_{osc} \ll L$. This case becomes the typical case with increasing L.

In either case, when E_{scat} approaches characteristic electronic energy level spacings Δ_0 in a molecule, the electron dynamics quickly becomes nonadiabatic. While the exact conditions for the onset of such behavior depend on the specific molecule, a simple semiquantitative estimate for a system with characteristic length L and level spacing Δ_0 can be obtained by considering a pair of states separated by Δ_0 and coupled by the transition matrix element $d_0 \sim L$.

The probability of nonresonant Landau-Zener–type nonadiabatic transition during one-half of the laser cycle is $\sim \exp(-\pi\Delta_0^2/4\omega_L\mathcal{E}L)$ [18]. When $\omega_L\mathcal{E}L \sim \Delta_0^2$, transitions are quickly saturated for virtually any pair of levels, leading to strong nonresonant absorption by all delocalized electrons. This regime, which represents a failure of both the quasistatic and single active electron pictures, can occur even when $\gamma < 1$ (formally a tunneling limit). The greater the length L, the easier it is to reach the limit $\omega_L\mathcal{E}L \sim \Delta_0^2$. For example, at $L = 13.5$ Å, $\Delta_0 = 4$ eV, and $\lambda = 700$ nm, we find that $\omega_L\mathcal{E}L = \Delta_0^2$ already at intensity $I \approx 5.6 \times 10^{12}$ W/cm^2, typical for strong field experiments. Because of fast saturation of all transitions, in this limit energy absorption becomes only weakly sensitive to laser intensity, consistent with results in Figs. 2a and 2b.

In conclusion, we have systematically studied the limits of the quasistatic tunnel ionization model in unsaturated linear hydrocarbons. The new ionization dynamics observed is due to NME excitations during the ionization process, and the transition from the quasistatic to NME ionization dynamics depends on delocalized electron path length L. For increasing L, the strong field dynamics of delocalized electrons can be dominated by NME even in the "tunneling limit" $\gamma \ll 1$, thus rendering popular quasistatic models inadequate. For large conjugated molecules, this behavior extends far into the infrared and affects all aspects of their strong field femtosecond dynamics. The resulting excitation and ionization lead to very strong fragmentation with important consequences for many applications of intense femtosecond pulses, from controlling molecular dynamics to mass spectrometry. Below the multiple ionization limit, NME allows for efficient excitation of various multielectron states, giving access to a rich variety of different fragmentation patterns and opening new avenues for the control of unimolecular reactions.

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