

Role of proton dynamics in efficient photoionization of hydrocarbon molecules

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We experimentally investigate the ionization mechanism behind the formation of remarkably high charge states observed in the laser-pulse-induced fragmentation of different hydrocarbon molecules by Roither *et al.* [*Phys. Rev. Lett.* **106**, 163001 (2011)], who suggested enhanced ionization occurring at multiple C-H bonds as the underlying ionization mechanism. Using multiparticle coincidence momentum imaging we measure the yield of multiply charged fragmenting ethylene and acetylene molecules at several intensities and pulse durations ranging from the few-cycle regime to 25 fs. We observe, at constant intensity, a strong increase of the proton energy with increasing laser pulse duration. It is shown that this is caused by a strong increase in the yield of highly charged parent molecular ions with pulse duration. Based on experimental evidence we explain this increase by the necessary population of precursor states in the parent ion that feature fast C-H stretch dynamics to the critical internuclear distance, where efficient ionization via enhanced ionization takes place. For increasing pulse duration these precursor ionic states are more efficiently populated, which leads in turn to a higher enhanced-ionization probability for longer pulses. Our work provides experimental evidence for the existence of a multiple-bond version of enhanced ionization in polyatomic molecules.

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I. INTRODUCTION

Creation of electronic wave packets of subfemtosecond duration, a prerequisite for imaging attosecond processes, is facilitated by the process of strong-field ionization that takes place within a short time window near the peaks of intense laser half-cycles. In contrast to atoms, for which this process is now relatively well understood, there are a number of characteristics and accompanying processes that render ionization of molecules much more complicated and make it an active field of research.

One striking difference is that the ionization rate in molecules sensitively depends on the orientation of the molecule with respect to the laser polarization axis, as well as on the character of the molecular orbital from which an electron is removed [1–8]. In addition, the electronic energy levels in molecules can be quite closely spaced such that, within a single-particle picture, ionization may not only take place from the highest occupied molecular orbital (HOMO), but also from lower-lying valence orbitals with a pronounced probability [9–14], especially when ionization from the highest-lying states is suppressed by unfavorable orientation of the orbital(s) with respect to the laser polarization direction.

Furthermore, an intense laser field can also drive the transfer of population to electronically excited states [15–21] from which ionization can proceed more easily during the subsequent field cycles. Excitation of a molecule or molecular ion can also be induced by electron recollision, a process originally discovered and studied for atoms [22–24]. Because excited states in a molecule or molecular ion can be dissociative, preparation of electronically excited states by the ionization process and/or by field-driven excitation occurring during the laser pulse may lead to fragmentation of the parent molecule [14,25]. For example, excitations due to removal of an electron from a lower-lying molecular orbital by electron recollision can be used to control fragmentation reactions of polyatomic molecules on the laser-subcycle time scale [26].

Finally, the impinging laser pulse may also trigger nuclear dynamics and chemical bond rearrangement processes, which might lead to a strongly varying ionization rate as the nuclear motion proceeds. One of the most striking manifestations of this effect is enhanced ionization (EI) [27,28], where at a critical internuclear distance R_c the ionization rate is strongly enhanced as compared to that at the equilibrium internuclear distance or that at an internuclear distance much larger than R_c . By the development of the concept of enhanced ionization it became possible to explain the reason why the kinetic energy of fragment ions recorded by Coulomb explosion imaging was considerably lower than the kinetic energy expected, when the Coulomb explosion takes place at the equilibrium position

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of the ground state electronic potential energy surface of the neutral parent molecule [29–33]. Since then, the EI mechanism has been investigated extensively for diatomic molecules, e.g., [34–37], as well as for triatomic molecules [38–41].

In this paper we describe the results of experiments that were performed with the aim of understanding the mechanism behind laser ionization leading to multiply ionized hydrocarbon molecules [42–45], and the possibility of extending our understanding of EI to polyatomic molecules. Specifically we study ionization of acetylene, C_2H_2 , and ethylene, C_2H_4 , molecules subject to near-infrared (~ 750 nm) laser pulses. As long as the stretch motion of the internuclear distances within a molecule is sufficiently fast, such that R_c can be reached within the duration of the laser pulse, highly charged parent molecules can be formed due to the greatly enhanced ionization rate at R_c . Therefore, EI can be suppressed by using pulse durations shorter than the time needed for the involved bonds to stretch to R_c . This has been experimentally demonstrated for the very fast nuclear motion in molecular hydrogen [35] and deuterium [46], as well as for the considerably slower nuclear motion in CO_2 [41]. In our experiments we employ laser pulses with durations τ (FWHM) ranging from the few-cycle (~ 4.5 fs) to the multicycle (25 fs) regime, and laser peak intensities between 2×10^{14} and 8×10^{14} W/cm².

We are particularly interested in the ionization dynamics behind the surprisingly high charge states observed by Roither *et al.* [42] for a series of hydrocarbon molecules (CH_4 , C_2H_4 , C_4H_6 , and C_6H_{14}). In Ref. [42] it was shown that with 27 fs laser pulses at 790 nm very high charge states (e.g., $\geq +13$ for C_4H_6) can be generated even at moderate intensities of a few 10^{14} W/cm². Molecular ions prepared at those high charge states decompose completely into atomic fragment ions such as protons with considerably large kinetic energy. Based on experimental evidence it was suggested that a new type of molecular ionization, namely, EI that proceeds through the removal of electrons simultaneously at more than one C-H bonds within a molecule, i.e., a multiple-bond EI mechanism, is responsible for the astonishing ionization behavior.

Simulations based on time-dependent density functional theory performed for CH_4 and C_4H_6 have confirmed the experimental findings that, as a result of the interaction with the laser pulse, these molecules completely disintegrate into atomic ions via a concerted all-at-once Coulomb explosion, resulting in the formation of protons with high kinetic energy and very similar energy values [43]. However, while the simulations confirmed the fragmentation dynamics and the origin of the high proton energies observed in the experiments [42], the proposed multiple-bond EI mechanism could not be conclusively confirmed.

Ionization to such high charge states obviously necessitates the involvement of electrons in inner-valence orbitals in the underlying ionization process. A recent theoretical study [44,45] used time-dependent Hartree-Fock (TDHF), restricted to one spatial dimension, to investigate the ionization mechanism that leads to the experimentally observed high charge states. The results obtained using a model potential of the acetylene molecule C_2H_2 with fixed nuclear positions, clearly revealed the existence of a critical C-H internuclear distance at which the ionization rate is strongly enhanced. When the C-H distance is set to the critical distance, the model predicted that

at a laser intensity of 14×10^{14} W/cm² ionization proceeds not only from the HOMO but also from HOMO-1 and HOMO-2, and that the electron charge density from the HOMO and HOMO-1 efficiently localizes at the positions of the protons, as required for the EI mechanism. In addition, the laser field strongly couples the HOMO-2 to the two higher-lying orbitals such that in total about six electrons are removed from the C_2H_2 molecule. Qualitatively similar ionization behavior was reported for three-dimensional TDHF simulations on acetylene [47], showing an enhanced-ionization rate when the C-H internuclear distance is stretched to about two times the equilibrium distance. Thus, the TDHF simulations support the multiple-bond EI mechanism proposed by Roither *et al.* [42].

II. EXPERIMENT

In our experiments, few-cycle laser pulses are generated by spectral broadening of 25 fs laser pulses with a spectrum centered at 790 nm from a Ti:sapphire laser amplifier system in a 1-m-long hollow-core glass capillary filled with neon at several atmospheres pressure. Temporal compression of the pulses after the capillary by several bounces from pairs of chirped mirrors and subsequently passing them through a pair of glass wedges for fine-tuning the dispersion results in a pulse duration of ~ 4.5 fs. The duration and intensity stability of the pulses are monitored on a shot-to-shot basis by a stereo-above-threshold ionization phase meter [48,49].

The pulse duration was varied by positively chirping the shortest pulses by propagating them through different amounts of fused silica. We confirmed that the results presented below are independent of the sign of the chirp of the pulses, by measuring some of the spectra with negatively chirped pulses with pulse durations up to about 10 fs. Furthermore, as can be seen in Fig. 1, in the multicycle pulse limit ($\tau \gtrsim 17$ fs) the results obtained with Fourier limited pulses of $\tau = 25$ fs are almost recovered.

The pulses are directed into a cold target recoil ion momentum spectroscopy [50] apparatus described previously [26,42,51], where they are focused by a spherical mirror with a focusing length of 60 mm into a supersonic gas jet of randomly aligned ethylene or acetylene molecules. The fragment ions resulting from the interaction of a single molecule with a single laser pulse are guided over a length of 5.7 cm to a position and time sensitive detector by a weak homogeneous electric field (9.4 V/cm), where the positions and times of flight of the fragments are recorded in coincidence. From this information the three-dimensional momenta of the respective fragment ions are calculated. From the recorded momenta of fragment ions we extracted background-free kinetic energy spectra of the protons that are ejected during the laser-molecule interaction by selecting all protons that are emitted towards the detector within a 90° cone [42].

The peak intensity of the pulses in the measurement chamber was adjusted by reflecting the beam off a thick fused silica block under different angles, thereby changing the pulse energy. Calibration of the peak intensity on target was done with an estimated precision of $\pm 10\%$ by separate measurements using single ionization of Ar atoms in circularly polarized light [52].

III. RESULTS AND DISCUSSION

A. Measured proton energy spectra

Measured proton energy spectra for different laser pulse durations and peak intensities are shown in Fig. 1 for both C_2H_2 and C_2H_4 . It can be seen for both molecules that, at a given laser intensity, the proton energy spectra extend to higher energies with increasing pulse durations. While for the shortest pulse duration of 4.5 fs, for ethylene, C_2H_4 , the proton energies do not significantly exceed 10 eV even at the highest intensity of $8 \times 10^{14} \text{ W/cm}^2$, the proton energies extend up to 25 eV when the pulse duration is increased to 17 fs. Further increasing the pulse duration to 25 fs does not lead to significantly higher proton energies. The proton energy spectra observed for acetylene, C_2H_2 , measured at an intensity of $3 \times 10^{14} \text{ W/cm}^2$ [Fig. 1(a)], exhibit a similar dependence on pulse duration as those for ethylene. However, their energy distributions are consistently shifted to higher

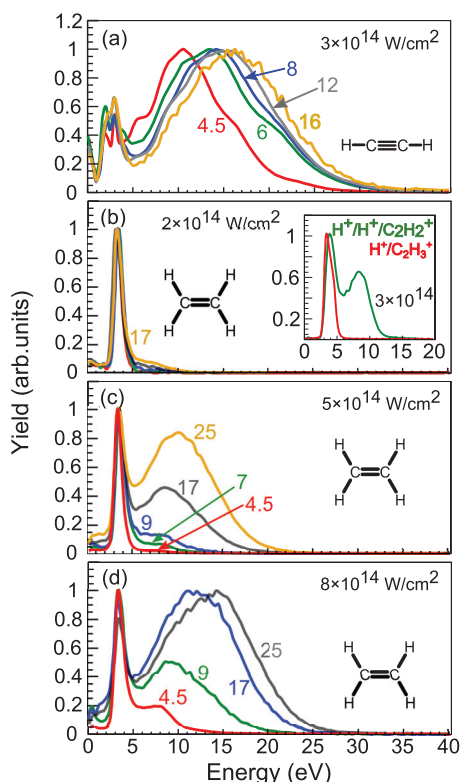


FIG. 1. (Color online) Measured energy spectra of protons ejected from acetylene (a) and ethylene [(b)–(d)] as a result of the interaction with laser pulses whose intensities and durations are indicated in the figures: For each of the spectra in the four spectral series the same laser peak intensity has been used, as indicated in each panel. Each spectrum is labeled with a pulse duration (FWHM) in femtoseconds and has been normalized to 1 at its respective maximum value around 10 to 20 eV [for acetylene, panel (a)], respectively at the spectral peak around 4 eV [for ethylene, panels (b)–(d)]. The inset in (b) shows for comparison the proton kinetic energy distributions of two fragmentation channels (as indicated), where the fragmentations start from doubly and triply charged ethylene, respectively, measured with a laser peak intensity of $3 \times 10^{14} \text{ W/cm}^2$ and a pulse duration of 4.5 fs.

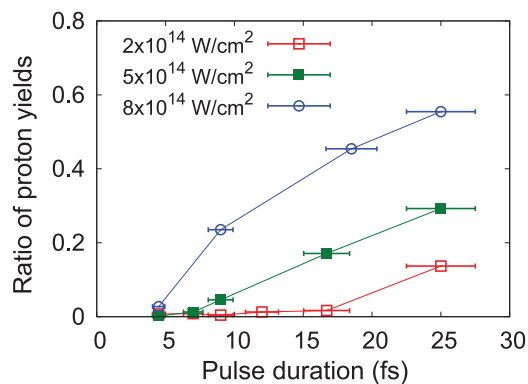


FIG. 2. (Color online) Ratio of integrals over the overall noncoincidence proton energy distributions for energies higher than 12 eV normalized to the integral over all proton energies (taken from Fig. 1) for C_2H_4 as a function of laser pulse duration for the three indicated intensities. The lines are only to guide the eye.

energies as compared to those for ethylene measured at the only slightly higher intensity of $5 \times 10^{14} \text{ W/cm}^2$ [Fig. 1(c)]. We will discuss this observation in more detail in the next section.

Energy distributions of protons created by Coulomb explosion of doubly and triply charged ethylene ions during two- and three-body fragmentations extracted by coincidence selection are shown in the inset of Fig. 1(b). By comparing these spectra to those measured for the 4.5 fs pulse in Fig. 1(d) it becomes evident that even at $8 \times 10^{14} \text{ W/cm}^2$ protons being ejected with low kinetic energies are dominantly formed through two- and three-body fragmentations of lower charge states. We have checked by coincidence analysis that only protons with an energy of $\gtrsim 12 \text{ eV}$, observed only for longer pulses, are ejected during complete fragmentation of the ethylene molecule into six ionic fragments from charge states equal to or higher than +6.

To investigate the dependence of the appearance of high charge states on the laser pulse duration, we plot in Fig. 2 the integral over the overall noncoincidence proton energy distributions for energies higher than 12 eV normalized to the integral over all proton energies, as a function of pulse duration and for different intensities. As can be seen, the clear trend is that the relative yield of higher charge states, i.e., the relative yield of higher proton energies, increases with pulse duration for all intensities. Quantitatively, however, the relative yield of high proton energies also depends on the laser peak intensity. These data suggest the existence of a mechanism that leads to an increasing probability of ionizing the molecule to charge states higher than +6 when the laser pulse duration becomes longer. Thus, the data in Fig. 2 are in agreement with the multiple-bond EI mechanism proposed in Ref. [42], which necessitates that the laser pulse duration is long enough, such that the stretch motion of the C-H internuclear distances to the critical internuclear distance R_c can be completed before the laser pulse starts to fade again. For shorter pulses the R_c of the C-H bonds is apparently reached less likely prior to the trailing edge of the laser pulse and the ionization proceeds less efficiently.

B. Charge-state selected proton spectra

In order to gain insight into the ionization dynamics that lead to the formation of highly charged C_2H_2 and C_2H_4 molecules, we performed a multiparticle coincidence selection of the recorded data in a similar manner as in Ref. [42]. For acetylene we were able to perform a complete four-body coincidence selection of all four atomic ions produced during the decomposition of the multiply charged acetylene parent ions into two protons and two carbon ions C^{m+}/C^{n+} with charge states m and n , respectively. For the decomposition of ethylene into six atomic ions we took advantage of the fact that the two carbon ions roughly fulfill momentum conservation, as has been shown in our previous study [42]. This permitted us to select a certain charge state of the ethylene parent molecular ion, $z = m + n + 4$, by gating on a certain combination of carbon ions C^{m+}/C^{n+} in coincidence with one proton, when the two carbon ions roughly fulfilled momentum conservation within a momentum mismatch of $|\Delta p_i| \leq 30$ a.u., $i = \{x, y, z\}$.

The kinetic energy distributions of protons ejected through four-body fragmentation of acetylene from charge states $z = +4$ to $z = +6$ resulting from this selection are plotted in Figs. 3(a)–3(c) for different pulse durations and an intensity of 3×10^{14} W/cm². The corresponding distributions for completely fragmenting ethylene from charge states $z = +6$ to $z = +8$ measured for two pulse durations and an intensity of 8×10^{14} W/cm² are shown in Figs. 3(d) and 3(e). Also shown are the sums of the charge-state separated distributions (black lines), and the overall noncoincidence kinetic energy distributions (gray lines). For ethylene, the high-energy part of the overall noncoincidence energy distributions is well reproduced by the sum of the charge-state separated spectra. Thus, the highest proton energies in the case of ethylene are apparently generated by ejection from ethylene parent ions with charge states $z = +6$ to $z = +8$. In contrast, for acetylene, the high-energy part of the noncoincidence proton spectrum is not completely reproduced by our decomposition into the individual contributions from charge states $z = +4$ to $z = +6$. Thus, the highest observed proton energies are obviously produced by ejection from charge states higher than those considered in our coincidence selection, consistent with the higher overall proton energy cutoff discussed above [panel (a) vs (c) in Fig. 1(a)]. This is a notable observation, since the laser pulse intensity used for the acetylene data in Fig. 3 is considerably smaller than the one used for ethylene (by almost a factor of 3). This might suggest that for a given pulse duration and intensity C_2H_2 reaches higher charge states than C_2H_4 . A possible explanation for the reason why acetylene is more efficiently ionized to high charge states than ethylene, is that the underlying ionization mechanism might be sensitive to the alignment of the C-H chemical bonds with respect to the laser polarization direction. For acetylene, both of the two C-H bonds can be aligned along the laser polarization direction, while for ethylene not all of the four C-H bonds can be aligned simultaneously. This explanation is in agreement with the previous theoretical study in Ref. [53], which predicts a sensitive dependence of EI on the alignment of the molecule with respect to the laser field direction. This issue will be the content of a future study using aligned molecules.

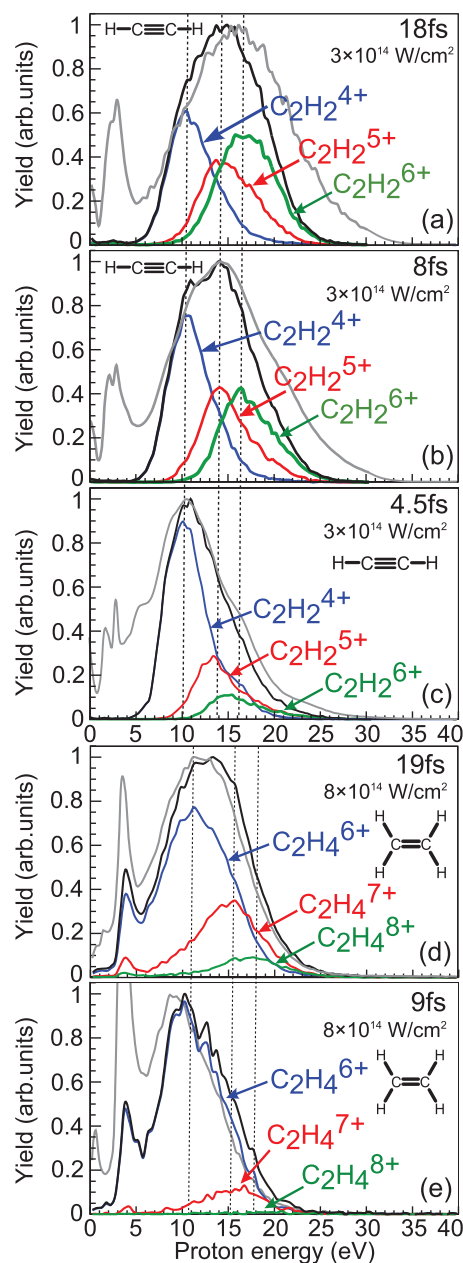


FIG. 3. (Color online) (a)–(c) Measured proton energy distributions of fragmenting acetylene. The gray lines show the overall noncoincidence distributions, normalized to 1 at their respective maxima around 10–15 eV. Colored lines show the spectra corresponding to ejection from charge states $z = 4, 5, 6$ during complete (four-body) fragmentation, and the black lines denote their sums normalized to the respective noncoincidence distributions in gray. The charge-state selected spectra, obtained by coincidence analyses as described in the text, are not corrected for their different detection efficiencies, which are estimated to differ by up to 10%. (d), (e) The same as in (a)–(c) but for complete (six-body) fragmentation of ethylene from charge states $z = 6, 7, 8$. The vertical dotted lines shall guide the eye in the comparison of the peaks of the charge-state selected proton spectra. The intensities and durations of the laser pulses are indicated in the figures.

Another important observation in Fig. 3 is that kinetic energy distributions of the protons ejected from a certain

charge state $z = m + n + 2$ of acetylene exhibit a smooth shape and that their center value monotonically increases with z . These features are consistent with a concerted Coulomb explosion dynamics of both protons sensing a very similar positive charge z , as has been shown in Refs. [42,43]. For ethylene the situation is similar, except that in the low-energy region below approximately 8 eV our coincidence selection is deteriorated by false coincidences. Thus, the shape of the charge-state selected proton energy distributions is less smooth, which is particularly pronounced for $z = +6$. The two most important features of the charge-state selected distributions in Fig. 3, however, are that for both molecules (i) the energies of the protons ejected from a certain charge state of the parent molecular ion are roughly independent of the pulse duration, and (ii) the yield of fragmenting from higher charge states monotonically increases with pulse duration.

C. Examination of C-H bond stretch dynamics

In the following we will investigate the two main findings revealed by Fig. 3 in detail. We will first discuss the dependence of the proton energies corresponding to a certain charge state of the parent molecular ion on the laser pulse duration. To this end we plot in Figs. 4(a) and 4(b) the mean kinetic energies of protons ejected from charge states $z = \{+6, +7, +8\}$ and $z = \{+4, +5, +6\}$ of ethylene and acetylene, respectively, as a function of pulse duration. In addition, we show for acetylene the same values also for two fragmentation channels starting from $z = +3$ [Fig. 4(b)]. It can be clearly seen that for both molecules the proton energies are almost independent of the pulse duration for a given charge state. As the energy released during the concerted proton ejection process driven by Coulomb repulsion is shared amongst all ejected protons (two for acetylene and four for ethylene), the protons ejected from acetylene feature a consistently higher energy for a given charge state than those ejected from ethylene. Under the assumption that the fragment ions are driven apart by pure Coulomb repulsion, the C-H internuclear distance R_{C-H} at which the proton ejection takes place, can be estimated from the mean kinetic energies of protons shown in Figs. 4(a) and 4(b). We performed such an estimation for acetylene. By adopting $R_{C-C} = 1.2 \text{ \AA}$, which is the equilibrium C-C internuclear distance of acetylene [54], using Eq. (1),

$$E = \frac{z - 2}{R_{C-H} + R_{C-C}/2} + \frac{1}{4(R_{C-H} + R_{C-C}/2)}, \quad (1)$$

R_{C-H} values were calculated from the observed mean values of the kinetic energy distributions of protons, E , shown in Fig. 4(a). In deriving Eq. (1) we assumed that the charge density on the C-C structure, $z - 2$, is concentrated as a point charge in the center between the two carbon nuclei. The results of this calculation are shown in Fig. 4(c). As can be clearly seen, the resulting R_{C-H} take almost the same values, roughly 2.5 times larger than the equilibrium C-H distance, for all laser pulse durations, which is consistent with the results expected from the enhanced-ionization mechanism suggested previously [42,44,45]. We envision the underlying ionization dynamics as follows. Starting with the first few ionization events that take place during the rising edge of the laser pulse, the C-H internuclear distance stretches to larger values,

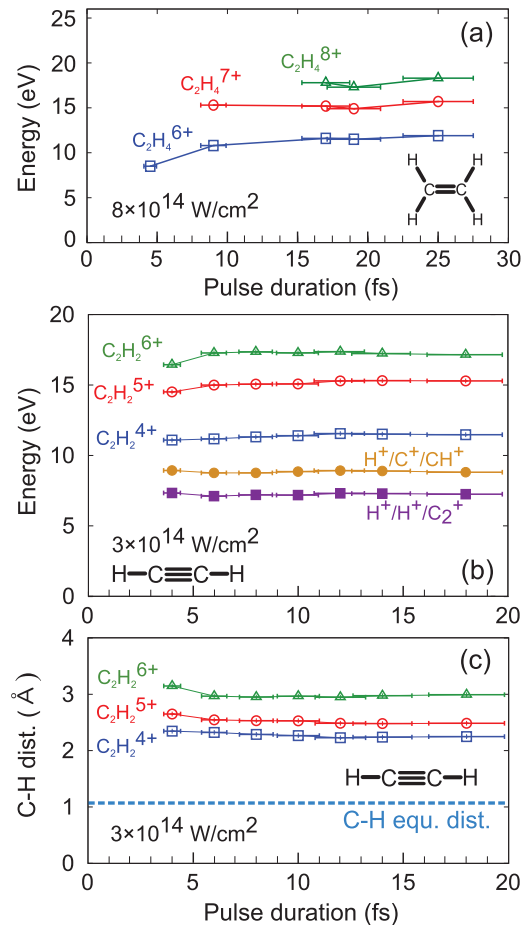


FIG. 4. (Color online) (a) Mean energy of protons ejected during complete fragmentation of ethylene parent molecular ions with a certain charge state (z , as indicated) as a function of pulse duration and a constant intensity of $8 \times 10^{14} \text{ W/cm}^2$. (b) The three uppermost data series show the same as (a) but for acetylene parent molecular ions and an intensity of $3 \times 10^{14} \text{ W/cm}^2$. The two lower data series, shown for comparison, are for protons ejected from the triply charged acetylene ion during breakage into three fragments. (c) C-H distance at the time of proton ejection calculated from the proton energies in (b), shown with the same data point style (see text for details).

and enhanced ionization takes place multiple times when the distance reaches the critical internuclear distance R_c within the laser pulse duration. The almost constant values of R_{C-H} shown in Fig. 4(c) suggest that the C-H stretch motion proceeds very rapidly so that the C-H distance can reach the critical distance within the laser pulse duration even for the shortest laser pulse duration of 4.5 fs. The results shown in Fig. 4, together with the findings described in Sec. III B, namely, that (i) the number of electrons removed from acetylene, having two protons, and ethylene, having four protons, reaches up to (at least) six and eight, respectively, and that (ii) all ejected protons exhibit very similar energy, suggest that all the C-H chemical bonds are subjected to the enhanced-ionization process, which may be called a multiple-bond EI process, as was proposed by Roither *et al.* [42] and theoretically interpreted by Lötstedt *et al.* [44,45].

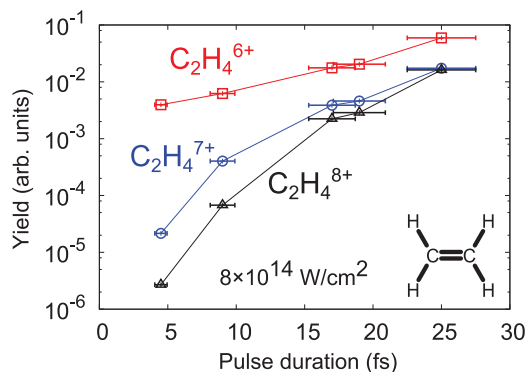


FIG. 5. (Color online) Yield of three completely fragmenting ethylene parent molecular ions with charge states $z = 6, 7, 8$ as a function of pulse duration measured at the indicated intensity, relatively normalized at each pulse duration to the number of laser shots and the estimated jet density.

D. Dependence of the proton kinetic energy on laser pulse duration

In order to discuss the origin of the strong dependence of the proton kinetic energies on the laser pulse duration shown in Fig. 1, we plot in Fig. 5 the dependence of the yield of the ethylene parent molecular ion on the laser pulse duration for charge states $+6$ to $+8$. The yield of the parent molecular ions with a given charge state $z = m + n + 4$, determined using three-body coincidence selections on the two carbon ions C^{m+}/C^{n+} in combination with one proton, as described above, has been normalized to the number of laser shots and the gas target density estimated from the backing pressure of the supersonic molecular jet at each pulse duration. It can be seen that the yields of all three charge states increase monotonically over several orders of magnitude when the pulse duration is increased from 4.5 to 25 fs, with higher charge states showing a steeper dependence on the pulse duration. While Fig. 5 shows yields for specific charge states, the kinetic energy distributions of protons shown in Fig. 1 originate from a mixture of parent ions in different charge states. For short pulse durations, the contributions from higher charge states are negligible, as shown in Fig. 5, and the detected protons are those ejected dominantly from parent ions with smaller charge states, resulting in low proton energies. In contrast, for longer pulse durations the contribution of the high charge states of the parent ions and therewith that of the protons ejected from them is large, leading to higher kinetic energy distributions of protons that appear as the high energy tails in Fig. 1. Thus, in sum, although highly charged molecular ions are formed by EI at the critical internuclear C-H distance R_c even when the pulse duration is short, as can be clearly seen in Fig. 4, the probability for EI is very small for the shorter pulse duration, leading to the observation that the yield of protons with higher kinetic energies is very small.

E. Role of the C-H stretch dynamics in the enhanced-ionization process

We have shown above that two findings are central in understanding the ionization process responsible for the proton

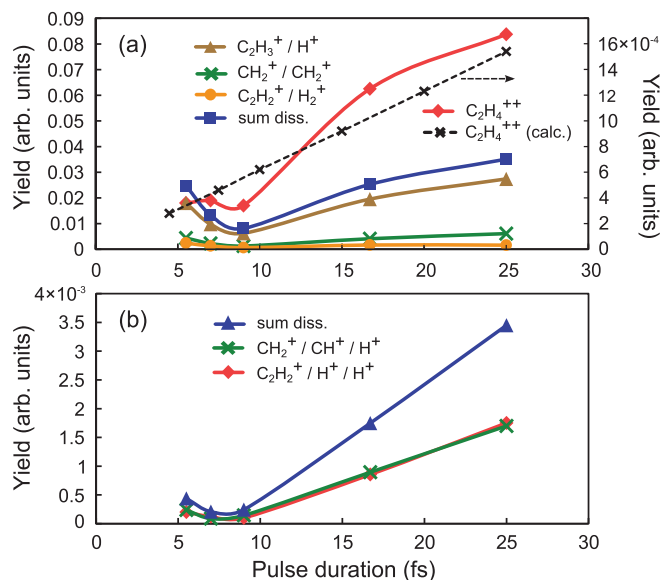


FIG. 6. (Color online) Yield of doubly (a) and triply (b) charged ethylene parent molecular ions as a function of pulse duration, measured at a peak intensity of 5×10^{14} W/cm², relatively normalized at each pulse duration to the number of laser shots and the estimated jet density. As $C_2H_4^{z+}$ with $z \geq +2$ is partly dissociative, the yield of all identified dissociating channels (separately and also summed up, as indicated in the figure) is shown. Due to different detection efficiencies the yields of different channels are not to be compared quantitatively. In (a) we also show the dependence of the yield of $C_2H_4^{2+}$ on the pulse duration calculated by tunnel-ionization theory (black dashed line, right axis applies); see text for details.

energy distributions in Fig. 1: First, multiple-bond EI at roughly 2.5 times the equilibrium value (Fig. 4), and secondly, the strongly increasing probability of reaching high charge states with increasing pulse duration (Fig. 5). Initiation of the C-H stretch motion to R_c critically depends on the preparation of the parent molecular ion in suitable states that feature such a stretch motion. We may call these states the precursor states and the corresponding molecular ions the precursor ions.

In order to investigate the initiation of the C-H stretch dynamics we plot in Fig. 6 the yields of doubly and triply charged ethylene parent molecular ions as a function of laser pulse duration for two different intensities. Doubly and triply charged ions can be regarded as example species for the precursor ions. Because doubly and triply charged ethylene ions may decompose into up to two and three fragment ions, respectively, we summed up the yields of all identified coincidence fragments for the fragmentation channels starting from the doubly and triply charged ions (see caption of Fig. 6 for details). Ionization to doubly and triply charged ethylene will take place during the leading edge of the laser pulse. Because field ionization takes place in bursts every laser half-cycle, for a given pulse intensity and molecular orientation and in the absence of saturation effects the yield of these ions should monotonically increase with the pulse duration. To illustrate this we have calculated the yield of $C_2H_4^{2+}$, assuming that the two electrons are removed sequentially, as a function of laser pulse duration at the experimental laser peak intensity using tunnel-ionization theory [55] and the tabulated

ionization potentials of ethylene [54], and taking ionization saturation into account, but neglecting effects caused by the structure of molecular orbitals [2,3]. The results of these calculations are shown by the black dashed line in Fig. 6(a). As can be seen, for the laser pulse parameters used in the experiment, the yield of $C_2H_4^{2+}$ is predicted to increase linearly with pulse duration due to saturation of single ionization. In contrast, it can be seen in Fig. 6 that, when the pulse duration is increased, the measured yields of the doubly and triply charged ions decrease significantly, reach a minimum around 9 fs, and then increase monotonically up to the longest pulse duration used in the experiments. The initial *decrease* in the yield of low charge states can be explained by saturation effects caused by an overproportionally strong *increase* of the yield of higher charge states z , most likely +4 and +5, but with a certain probability also the charge states $z \geq +6$ plotted in Fig. 5. Such an overproportional increase of the probability of higher charge states with pulse duration is very unlikely to be observed for field ionization at $R_{C-H} \ll R_c$. Rather it can be considered evidence of the increasing probability for EI: As the pulse duration increases to $\tau \approx 9$ fs, the probability that the C-H bonds reach the critical internuclear distance R_c strongly increases. Accordingly, as at R_c the ionization probability is significantly higher than the one for $R_{C-H} \ll R_c$ or $R_{C-H} \gg R_c$, the fraction of molecules that will be further ionized also strongly increases, which manifests itself in the observed decrease of the yield of charges states +2 and +3 (cf. Fig. 6). At $\tau \approx 9$ fs the pulse duration seems to be sufficiently long such that the critical C-H bond length R_c can be reached by almost all of the weakly ionized precursor ions. Consequently, the increase in the yield of charge states higher than +3 is no longer overproportionally high, but follows the increase in yield of the precursor ions. Therefore, from this pulse duration on the yield of the latter monotonically increases in accordance with (saturated) conventional field ionization. In agreement with the described scenario, we note that in Fig. 5 the slope of the increase in yield with pulse duration becomes somewhat reduced at $\tau \approx 9$ fs for the highest charge states.

IV. SUMMARY AND OUTLOOK

The results of the experiments described here offer further evidence for the existence of a multiple-bond version of EI in polyatomic molecules—a mechanism recently proposed by Roither *et al.* [42] and theoretically interpreted by Lötstedt *et al.* [44,45].

We show by means of multiparticle coincidence analysis that the C-H internuclear distances of highly charged acetylene, derived from the proton energies by a simple model, take almost the same values independent of the laser pulse duration. Qualitatively comparable results are obtained for ethylene. This means, that with a certain probability the C-H bonds can stretch to the critical internuclear distance even during a pulse duration as short as 4.5 fs.

We also show that the yields of highly charged ethylene increase significantly as the laser pulse duration increases.

This shows that for short pulse durations the molecular ions are mainly put to lower charge states, and only for longer pulse durations are they efficiently put to high charge states. This pulse duration dependence of the yield allows explaining the observed monotonic increase of the energy cutoff in the proton spectra (Fig. 1). We explain the strong dependence of the yield on the pulse duration by the necessary population of precursor states that feature fast C-H stretch dynamics to the critical internuclear distance, where efficient ionization via EI takes place. For increasing pulse duration these precursor states are more efficiently populated, which leads in turn to a higher probability of EI for longer pulses. We take as evidence for this explanation the depletion of the yields of the lower charge states of ethylene up to a laser pulse duration of around 9 fs (Fig. 6).

Our work, hence, reveals, in addition to providing further evidence for the multiple-bond enhanced-ionization mechanism, another interesting point: The efficiency of ionization of hydrocarbon molecules to high charge states can be controlled by controlling the population of electronic states of parent ions that feature fast C-H stretch motion, such as dissociative excited electronic states. Considering that such electronic states can be populated by removal of electrons from lower-lying occupied valence orbitals, control of highly efficient ionization can therewith be implemented by controlling the removal of electrons from specific lower-lying valence orbitals. As has been shown recently, this can be achieved using the carrier-envelope phase of few-cycle pulses [26] as the control parameter. Another control parameter would be the alignment of the molecular axis with respect to the laser polarization direction. Thus, molecular alignment offers a possibility for the further investigation of the coupled electronic and nuclear dynamics that underlie the highly efficient ionization of polyatomic molecules [42,43].

Finally, even though the multiparticle coincidence experimental data recorded as a function of pulse duration presented here offer additional clear evidence for the existence of a multiple-bond version of EI, a more direct investigation of the underlying coupled electronic and nuclear dynamics could potentially be achieved by direct time-resolved probing with still shorter, subfemtosecond pulses in the XUV wavelength range, for example, by a transient absorption scheme [56].

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