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# Time-dependent density functional study of the alignment dependent ionization of acetylene and ethylene by strong laser pulses

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The alignment dependent ionization of acetylene and ethylene in short laser pulses is investigated in the framework of the Time-Dependent Density Functional Theory coupled with Ehrenfest dynamics. The molecular alignment is found to have a substantial effect on the total ionization. Bond stretching is shown to cause an increase of the ionization efficiency, i.e. enhanced ionization, in qualitative agreement with previous theoretical investigations. It is also demonstrated that the enhanced ionization mechanism greatly enhances the ionization from the inner valence orbitals, and the ionization of the inner orbitals is primarily due to their extended weakly bound density tails.

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## I. INTRODUCTION

The ionization of molecules with intense laser pulses is a complex process due to the interplay of the time varying external potential introduced by the strong laser electric field and the Coulomb interaction between the electrons [1–6]. The final and seemingly close aim is not only understanding but also controlling the ionization dynamics to influence chemical reactions at the femtosecond time scale [7–10]. The interaction of molecules with laser fields obviously depends on the laser parameters such as field strength, frequency, pulse shape and carrier envelope phase. It also depends on the directionality of the molecular frame relative to the laser field's polarization axis, which will hereafter be referred to simply as the alignment. Over the last decade experimental investigation of photoelectron angular distributions from aligned molecules has become possible [11–15]. This allows a clear comparison between experiment and theory without the obscuring effect of averaging over alignments [16]. Experiments also reveal a difference in the ionization from different molecular orbitals reflecting the nodal symmetry of the molecular wave functions [17–26]. Beyond mere structural effects it is also found that the total ionization yield can be increased by a coherent amplification of lower orbitals [19]. Finally, one of the most important mechanisms in molecular ionization is enhanced ionization [27–29], where highly efficient ionization occurs at critical nuclear separations. Recently, experimental evidence has been found that this process may also take place at many bonds in parallel in a polyatomic molecule [30, 31].

In this paper the Time-Dependent Density Functional Theory [32] coupled with the Ehrenfest dynamics [33] will be used to study the alignment dependence of ionization in short laser pulses. Two small molecules, acetylene and ethylene, exposed to laser pulses of various intensity and durations will be used to analyze how the time-dependent Kohn–Sham orbitals' ionization dynamics couple with the ions' dynamics. We will study (i) the enhanced ionization in a restricted fixed ion model as well as in a fully dynamical simulation (ii) the alignment dependence of the ionization, and (iii) the role of the molecular orbitals and their different symmetries in the ionization and fragmentation dynamics.

From a numerical point of view these are difficult problems because the solution of the time-dependent Schrödinger equation is very complicated beyond simple one- or two-electron systems. Pioneering works aiming to set up a simple framework to understand ionization include the model where the electrons and nuclei are treated classically [29], and the single active electron model [34], originally formulated for atoms, which as-

sumes that the ionization of atoms can be described by an appropriately modified hydrogen-like model. This model was later extended for molecules [35] and has been used to study the ionization of diatomic molecules [36, 37]. Another theoretical approach, the Time-Dependent Hartree Fock (TDHF) [38–40] method, was also used to study the physical mechanisms behind the fragmentation of molecules in intense laser fields. These works have focused on the total and orbital ionization efficiencies and the enhanced ionization mechanism of acetylene ( $C_2H_2$ ) by exploring the electron dynamics.

Enhanced ionization is described as a three step process [29]. First the C-H bonds expand to a critical separation,  $R_c$ . Then, the increased C-H bond length leads to highly efficient ionization of the molecule [30, 31]. After the enhanced ionization, the molecule often undergoes fragmentation ejecting the hydrogen ions. Using the TDHF approach it was shown that as the C-H bond lengths are symmetrically increased, the ionization efficiency of each orbital also increases until the bond lengths reach a critical separation after which the ionization efficiency plateaus, thus demonstrating the enhanced ionization mechanism. The TDHF approach is expected to capture the essence of the laser induced electron dynamics. However, in these simulations the ion positions were fixed for the duration of the laser pulse.

A dynamically more complete picture of the electron-nuclear dynamics and ionization can be given in the framework of TDDFT. TDDFT has been used to study the Coulomb explosion of deuterium [41, 42], biomolecules immersed in liquid water [43], water clusters [44], and small hydrocarbon molecules [16]. TDDFT simulations have also been used to describe the electron-ion dynamics of  $H_2S$  [45] and to simulate the Coulomb imaging of biphenyl [46].

The plan of this paper is as follows. After this introduction we briefly describe the computational approach in section II. Section III. presents the results and analysis of the ionization mechanisms of the acetylene and ethylene molecules for different alignments and laser fields. The paper is closed with a summary in section IV.

## II. COMPUTATIONAL METHOD

The electron dynamics of the simulation were modeled using Time Dependent Density Functional Theory (TDDFT) on a real-space grid with real-time propagation. Core electrons, which are difficult to handle computationally, were represented using norm-conserving Troullier-Martins pseudopotentials [47].

In the first stage of the calculation the initial (ground) state of the system is prepared by performing the ground-state DFT calculation. Next, the time-dependent Kohn–Sham orbitals,  $\psi_k$ , are determined by solving the time-dependent Kohn–Sham equation

$$i\hbar \frac{\partial \psi_k(\mathbf{r}, t)}{\partial t} = H \psi_k(\mathbf{r}, t), \quad (1)$$

where  $k$  is a quantum number labelling the orbital. The (Kohn-Sham) Hamiltonian is given by

$$H = -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V_{\text{H}}[\rho](\mathbf{r}, t) + V_{\text{XC}}[\rho](\mathbf{r}, t) + V_{\text{ext}}(\mathbf{r}, t). \quad (2)$$

Here  $\rho$  denotes the electron (number) density, which is defined by a sum over all occupied orbitals:

$$\rho(\mathbf{r}, t) = \sum_{k=1}^{\infty} f_k |\psi_k(\mathbf{r}, t)|^2, \quad (3)$$

where  $f_k$  is the occupation number of the orbital  $\psi_k$ .  $f_k$  may take on the values 0, 1, and 2 ( $f_k = 2$  is permitted via spin degeneracy).  $f_k$  is subject to the constraint  $\sum_{k=1}^{\infty} f_k = N$ , where  $N$  is the total number of (valence) electrons in the system.

$V_{\text{H}}$  in (2) is the Hartree potential, defined by

$$V_{\text{H}}(\mathbf{r}, t) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}, \quad (4)$$

and accounts for the electrostatic Coulomb interactions between electrons.

$V_{\text{XC}}$  is the exchange–correlation potential, whose exact form is a complicated functional of the entire history of the electron density. It will be approximated using the adiabatic local–density approximation (ALDA) with the parameterization of Perdew and Zunger [48].

The last term in (2),  $V_{\text{ext}}$ , is the external potential, which includes the implicitly time–dependent potential due to the ions,  $V_{\text{ion}}$ , and the explicitly time–dependent potential due to the electric field of the laser  $V_{\text{laser}}$ .  $V_{\text{ion}}$  is a sum of norm-conserving pseudopotentials by Troullier and Martins [47] centered at each ion.

$V_{\text{laser}}$  is described using the dipole approximation,  $V_{\text{laser}} = \mathbf{r} \cdot \mathbf{E}(t)$ , with the time–dependent electric field given by,

$$\mathbf{E}(t) = \hat{\mathbf{k}} E_{\text{max}} \exp \left[ -\frac{(t - t_0)^2}{2a^2} \right] \sin(\omega t). \quad (5)$$

The parameters  $a$ ,  $t_0$ , and  $E_{\text{max}}$  define the width, initial position of the center, and the maximum amplitude of the Gaussian envelope, respectively.  $\omega$  describes the frequency of the laser, and  $\hat{\mathbf{k}}$  is a unit vector defining the polarization of the electric field.

The time–dependent orbitals, from which the electron (number) density is calculated, may be formally time–propagated from the initial state to some time,  $t$ , by using the time–evolution operator,

$$U(0, t) = \mathcal{T} \exp \left[ -\frac{i}{\hbar} \int_0^t H(\mathbf{r}, t') dt' \right], \quad (6)$$

where  $\mathcal{T}$  denotes time ordering. In practice,  $U(t, 0)$  is split into a product of multiple time–evolution operators, each corresponding to a short time step  $\delta t$ ,

$$U(0, t) = \prod_q U(t_q, t_q + \delta t), \quad t_q = q\delta t. \quad (7)$$

in our calculations,  $U(t_q, t_q + \delta t)$  is approximated using a fourth–order Taylor expansion, so that the propagation of the Kohn–Sham orbitals over a very short time step,  $\delta t$ , is given by,

$$\psi_k(\mathbf{r}, t_q + \delta t) \approx \sum_{n=0}^4 \frac{1}{n!} \left( -\frac{i\delta t}{\hbar} H(\mathbf{r}, t_q) \right)^n \psi_k(\mathbf{r}, t_q). \quad (8)$$

The Taylor–propagation, though not unconditionally stable, gives a very stable propagation provided that the time step is chosen to be suitably small. The advantage of the Taylor–propagation is that it is very simple as it only requires the repeated action of the Hamiltonian on the wave function. A review and comparison of the advantages and disadvantages of different time propagating schemes in TDDFT can be found in Ref. [49].

In real space TDDFT the Kohn–Sham orbitals are represented at discrete points in real space. In practice these discrete points are organized in a uniform rectangular grid. The accuracy of numerical calculations is controlled by adjusting the grid spacing. At the walls of the simulation cell boundary conditions must be enforced. Typically the wavefunctions are set to zero at the walls. However, this zero–boundary condition can lead to an unphysical reflection of the wavefunction off the walls of the simulation cell. To prevent this from happening we implemented a complex absorbing potential (CAP). This potential is nonzero only in the region of space close to the walls. The functional form of the CAP used in our simulations is taken from Manolopoulos [50]. This negative, imaginary CAP is derived from a physically motivated differential equation and its form is

$$-iw(x) = -i \frac{\hbar^2}{2m} \left( \frac{2\pi}{\Delta x} \right)^2 f(y) \quad (9)$$

where  $x_1$  is the start and  $x_2$  is the end of the absorbing region,  $\Delta x = x_2 - x_1$ ,  $c = 2.62$  is a numerical constant,  $m$  is the electron’s mass and

$$f(y) = \frac{4}{c^2} \left( \frac{1}{(1+y)^2} + \frac{1}{(1-y)^2} - 2 \right), \quad y = \frac{(x - x_1)}{\Delta x}. \quad (10)$$

As the molecule is ionized by the laser field, electron density will travel to the edge of the simulation box where it is absorbed by the CAP. The integral of the electron density over the volume of the box,

$$N(t) = \int_V \rho(\mathbf{r}, t) d^3x, \quad (11)$$

will therefore diverge from the initial electron number,  $N(0)$ . Since, in general,  $N(t)$  is not an integer, we will



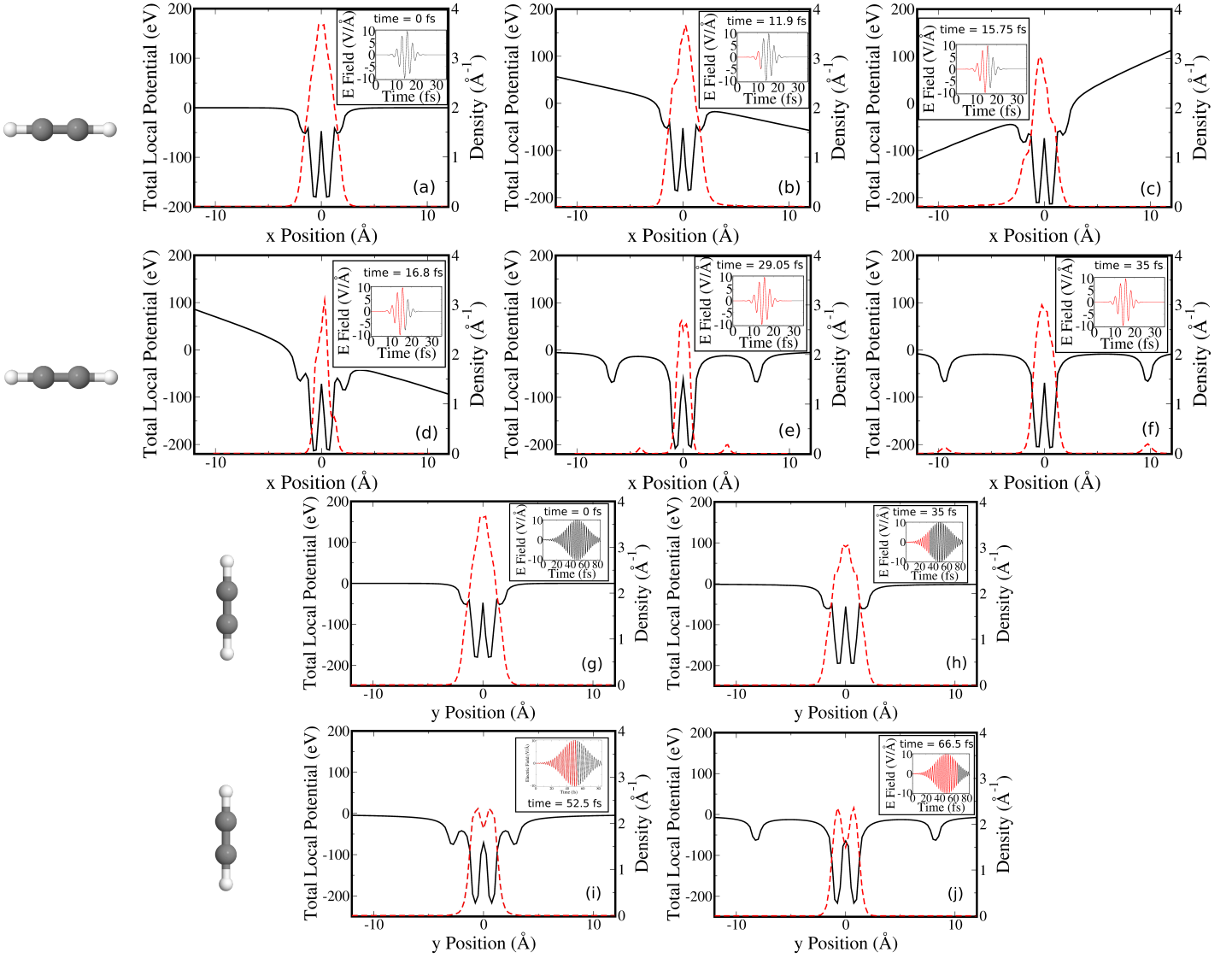


FIG. 1. (Color online) (a)-(f) Selected snapshots of the total local potential (solid black line) and the density (dashed red line) for C<sub>2</sub>H<sub>2</sub> along the alignment axis of the molecule ( $x$  axis), integrated out to 2 Å perpendicular to the  $x$  axis. The laser peak intensity is  $14 \times 10^{14}$  W/cm<sup>2</sup> and the pulse duration 4.5 fs. The total local potential consists of the Hartree potential, the local part of the exchange correlation potential, the ionic pseudo-potential, and the external potential of the laser field. The insets show the simulation time and the laser pulse highlighted up to the current simulation time. Panel (a) shows the unperturbed initial state. In (b) the density spreads towards one end of the simulation box due to the external potential. In (c) the electric field has switched direction and the density spreads towards the opposite end of the simulation box. In (d), the electric field has switched direction again. In panels (e) and (f) the hydrogen atoms have been split off and are ejected towards the ends of the simulation box. (g)-(j) Selected snapshots of the total local potential (solid black line) and the density (dashed red line) along the alignment axis of C<sub>2</sub>H<sub>2</sub> ( $y$ ), integrated out to 2 Å perpendicular to the  $y$  axis. The laser polarization direction is  $x$ , the peak intensity is  $14 \times 10^{14}$  W/cm<sup>2</sup> and the pulse duration is 25 fs. Panel (g) shows the unperturbed initial state at. In panel (h) the density has decreased as the laser ionizes the molecule. In panel (i) the density has further decreased and the hydrogen ions have begun to dissociate from the molecule. In panel (j) the hydrogen ions have dissociated and are ejected towards the ends of the simulation box.

refer to it henceforth as the fractional electron number. We interpret  $N(0) - N(t)$  as the total ionization of the molecule.

Motion of the ions in the simulations is treated classically based on the Ehrenfest theorem [33]. The quantum

forces on the ions, which are due to the electrons, are given by the derivatives of the expectation value of the total electronic energy with respect to the ionic positions. These forces are then fed into Newton's Second Law, giv-

## A. C<sub>2</sub>H<sub>2</sub>

ing

$$M_i \frac{d^2 \mathbf{R}_i}{dt^2} = Z_i \mathbf{E}_{\text{laser}}(t) + \sum_{j \neq i}^{N_{\text{ions}}} \frac{Z_i Z_j (\mathbf{R}_i - \mathbf{R}_j)}{|\mathbf{R}_i - \mathbf{R}_j|^3} - \nabla_{\mathbf{R}_i} \int V_{\text{ion}}(\mathbf{r}, \mathbf{R}_i) \rho(\mathbf{r}, t) d\mathbf{r}, \quad (12)$$

where  $M_i$  and  $Z_i$  are the mass and pseudocharge (valence) of the  $i$ -th ion, respectively, and  $N_{\text{ions}}$  is the total number of ions.

The computational results presented in the next section have been calculated by using the following parameters. The  $L_x \times L_y \times L_z$  box size is  $L_x = 40$  Å,  $L_y = L_z = 34$  Å, for C<sub>2</sub>H<sub>4</sub> and  $L_x = L_y = L_z = 34$  Å for C<sub>2</sub>H<sub>2</sub>. The C-C bond lies in the  $x$  direction. The grid spacing is 0.25 Å in each direction. The CAP starts 5 Å from the boundary. The time step for the propagation of the wave function is  $\delta t = 0.0007$  fs. The equation of the ionic motion (Eq. (12)) is solved with the Verlet algorithm with time step 0.0028 fs. These parameters lead to very well converged results. The calculated ionization potential is 11.0 eV for C<sub>2</sub>H<sub>4</sub> and 11.8 eV for C<sub>2</sub>H<sub>2</sub> (the experimental values are 10.5 eV for the C<sub>2</sub>H<sub>4</sub> and 11.4 eV for C<sub>2</sub>H<sub>2</sub> [51]).

## III. RESULTS AND ANALYSIS

Using the Time-Dependent Density Functional Theory [32] and Ehrenfest dynamics [33] we have studied the ionization mechanism of acetylene and ethylene exposed to laser pulses carried at a wavelength of 800 nm with a various peak intensities and durations. Our choice of the two molecules is on the one hand motivated by previous experimental [30, 31] and theoretical [38–40] studies on these molecules and on the other hand by the different complexity and structure of them. The acetylene molecule is one step from the diatomic molecules towards more complicated structures. It is still a linear molecule, so the relative direction of the laser field and the molecular frame is given by a single angle, but it has two nonequivalent bonds: the strong threefold C-C bond in the middle and the two C-H bonds at the ends. Ethylene is one step further toward the larger hydrocarbon molecules. It has a coplanar geometry with a H-C-H angle close to the ideal 120° for sp<sup>2</sup> hybridized carbon. We will study the ionization from different orbitals, the dependence of ionization on the alignment of the molecule, and the ionization from bond-stretched configurations. The goal of this study is to understand the enhanced ionization mechanism beyond the static TDHF picture and to investigate the role of the molecular alignment in the ionization process.

The ionization and molecular dynamics of acetylene, C<sub>2</sub>H<sub>2</sub>, has been studied by varying the intensity and duration of the laser field for parallel and perpendicular alignments of the molecule relative to the laser polarization direction. We have studied the response to nine different laser fields (see Table I) with intensities and pulse durations typical in experiments [31].

### 1. Acetylene in a laser field polarized parallel to the molecular axis

Before turning to the detailed results of the TDDFT simulations we show a simple picture that captures the essence of the electron-nuclear dynamics in acetylene aligned parallel to the laser field polarization direction. In this picture we investigate the separate actions of the different potentials, i.e. Hartree potential [Eq. (4)], the local part of the exchange correlation potential, the ionic potential, and the external potential of the laser field. Fig. 1 shows snapshots at different times during and after the laser pulse of the total potential, i.e. the sum of all the potentials, and the electron density along the  $x$  axis, to which both the molecule and laser field polarization are parallel.

The total potential shows two shallow and two deep wells corresponding to the positions of the hydrogen and carbon nuclei. The acetylene molecule is subject to a few-cycle laser pulse with a duration of 4.5 fs and a laser peak of  $14 \times 10^{14}$  W/cm<sup>2</sup>. Here and throughout the manuscript the pulse duration is defined as full width at half maximum (FWHM) of intensity. In the second snapshot, Fig. 1(b), the potential declines and the tail of the density spreads out to the right. Next, Fig. 1(c), the laser field changes direction, the potential inclines and the density tail spreads out more towards the left side. At this time (15.75 fs) the laser has reached its peak amplitude and the hydrogen nuclei are already moving outward, although the distance from the original position is only 0.3 Å. The next snapshot, Fig. 1(d), illustrates the situation at the next peak of the laser. In these snapshots one can also compare the laser potential to the potential of the atomic cores and one sees that the ionization is more probable from and around the shallow hydrogen nuclei. The snapshots also show the ionization by the visible decrease of the total density. The number of valence electrons drops from 10 to 6 by the end of the laser pulse, see Fig. 3(a). The last two snapshots depict the potential and the density after the laser pulse, showing the motion of the emitted protons.

The motion of the nuclei and the eventual fragmentation is caused by the interplay of the forces arising from the electron localization caused by the laser and the direct force that the laser imposes on the charged nuclei. The latter force is given by the first term on the right-hand side of Eq. (12). The resulting forces on the H<sup>+</sup>

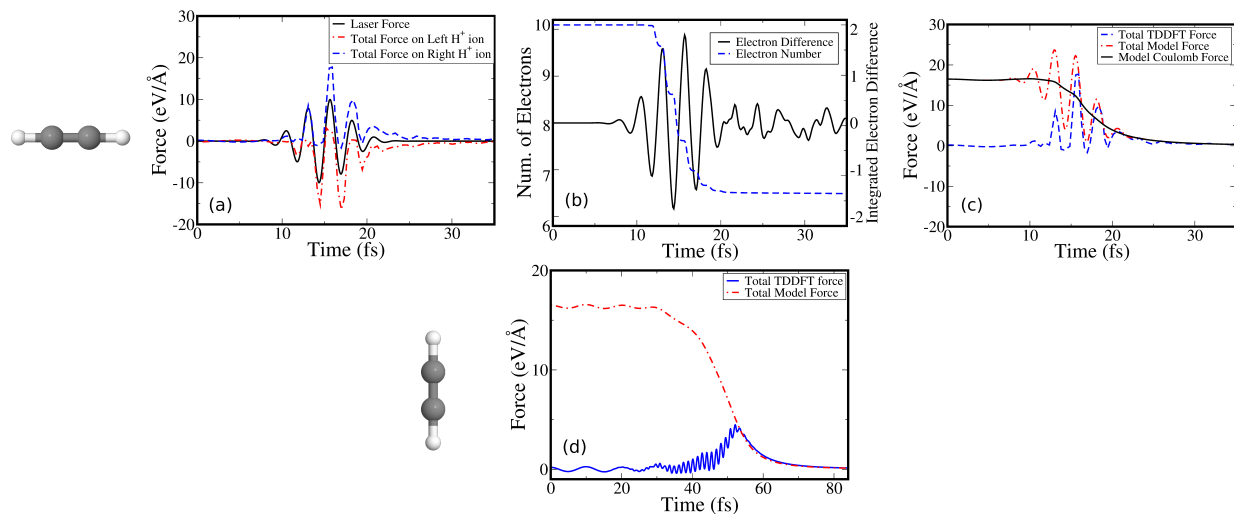


FIG. 2. (Color online) (a)-(c) Acetylene in a laser field with a polarization direction parallel to the molecular axis, an intensity of  $14 \times 10^{14}$  W/cm<sup>2</sup> and a pulse duration of 4.5 fs. (a) The total force on the two hydrogen ions, which is the sum of the laser force, the ion-ion forces, and the electron-ion force. The laser force (black line) is equal for both hydrogen ions. (b) Fractional electron number,  $\int \rho d^3x$ , and the difference between the fractional electron number in the left side of the box and the right side of the box,  $\int_{x<0} \rho d^3x - \int_{x>0} \rho d^3x$ . (c) The Coulomb force and total force on the right hydrogen ion calculated assuming a simple model where each atom loses one electron instantaneously. The ion-ion distances used in this simple force calculation are taken from the TDDFT simulation. The total force from the TDDFT simulation is shown for comparison. (d) The total force along the  $y$  (molecular) axis on a hydrogen ion calculated by TDDFT for a laser field polarized along  $x$  (perpendicular alignment) and a pulse peak intensity of  $14 \times 10^{14}$  W/cm<sup>2</sup> and pulse duration of 25 fs. A simple model calculation for the Coulomb force on a hydrogen ion is also shown, with the same details as in plot (c). The ion moves essentially along the  $y$  (molecular) axis for the duration of the simulation with only a small oscillation ( $< 0.02$  Å) along the  $x$  (polarization) axis.

ions are illustrated in Fig. 2(a). Consider the peak of the laser field at 15.75 fs. The laser field's polarization points to the right and it applies a rightward force on the two hydrogen ions. However, the laser also causes the fast moving electrons to move to the left, as shown in Fig. 2(b). For the left hydrogen ion, the excess of electrons will induce additional Coulomb shielding between the  $H^+$  and the other ions, which manifests as a leftward force. This force cancels with the laser force, and the total force is nearly zero. For the right hydrogen atom, the reduction of electrons reduces the Coulomb shielding, which manifests itself as a rightward force. This force will be additive with the laser force. Hence, the total force is much greater than the laser force alone. This picture is reversed when the electric field's polarization is reversed.

We have also compared the force acting on the protons to a model force [29], which is calculated as the sum of the direct laser force and the Coulomb force between a proton and a triply charged  $C_2H$  fragment. This quantity over time is depicted in Fig. 2(c). In the model force calculation the trajectory of the TDDFT simulation is used for the position of the particles and one electron is removed from each atom corresponding to the ionization of roughly four electrons shown in Fig. 2(b). As shown in Fig. 2(c), the sudden ionization leads to the removal of four electrons right after the peak of the laser field (around 17 fs) and after that time the model and TDDFT force are similar. The Coulomb dissociation starts at

around the peak of the laser field and at 17 fs the protons have moved about 2 Å. Hence, the bond is definitely broken and the simple Coulomb model captures the dynamics.

Now we turn to a more detailed analysis of the ionization mechanism using the full TDDFT model and allowing the ions to move according to the Ehrenfest dynamics. Before we begin this discussion we note that due to the Ehrenfest scheme each simulation represents only an averaging over all possible nuclear fragmentation channels. At low intensity and pulse width the probability of fragmentation is small and the dissociation of the C-H bonds does not occur in our simulations. Coulomb explosion is observed for higher intensities and longer pulses (see Table I).

We first consider the case of 4.5 fs laser pulses with three different peak intensities. The total ionization is plotted in Fig. 3. As expected, the number of electrons removed increases with the intensity of the laser. After the ionization exceeds a critical electron number the molecule undergoes Coulomb explosion.

Fig. 4 shows the ground state Kohn-Sham orbitals of acetylene and snapshots of the orbitals at the peak of the laser field. The HOMO and HOMO-1 are energy degenerate and their shapes are exactly 90° rotations of one another. The HOMO-2, HOMO-3, and HOMO-4 are all cylindrically symmetric, but each has its own nodal symmetry. Due to their different symmetries, the or-

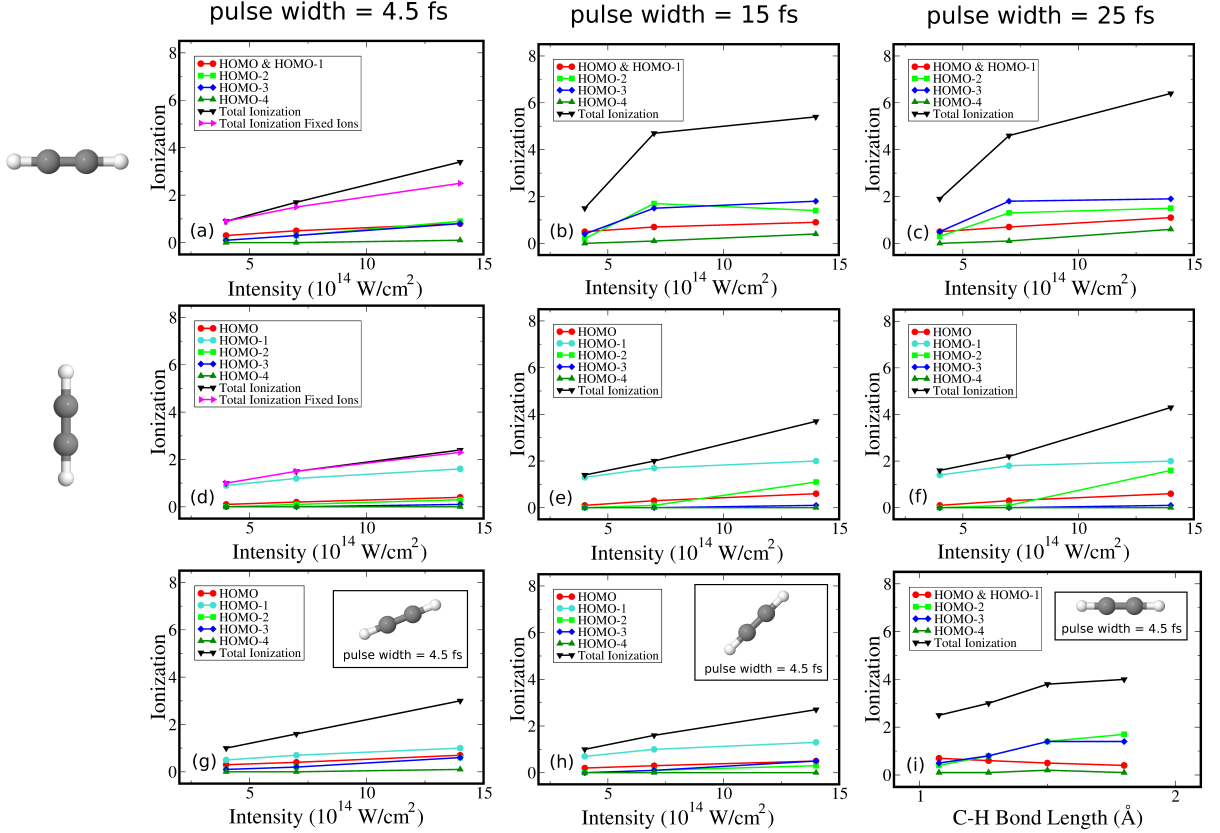


FIG. 3. (Color online) (a)-(f) Total and orbital ionization as a function of laser intensity for  $C_2H_2$  for a pulse duration of 4.5 fs (a, d), 15 fs (b, e) and 25 fs (c, f) for alignments of the molecule parallel (a)-(c) and perpendicular (d)-(f) to the laser polarization direction. Additionally, in panels (a) and (d) the total ionization for fixed ions is shown. Panels (g) and (h) show the total and orbital ionization as a function of laser intensity for angles of  $22.5^\circ$  and  $45^\circ$  between the molecular axis and laser polarization direction, respectively. The laser pulse duration is 4.5 fs. Panel (i) shows the ionization as a function of C-H bond length for a laser peak intensity of  $14 \times 10^{14} \text{ W/cm}^2$  and a pulse duration of 4.5 fs.

bitals each ionize with a different angular distribution (right column of Fig. 4). Despite the orbitals' different nodal symmetries, single particle energies, and angular distributions, the total ionization is very similar for the HOMO, HOMO-1, HOMO-2, and HOMO-3, see Fig. 3(a). The HOMO-4 orbital is significantly more deeply bound and the ionization is small. The ionization from the HOMO and the HOMO-1 orbitals is nearly identical due to their energy degeneracy and similar symmetry. At low intensity, the HOMO and HOMO-1 are the most ionized. As the intensity of the laser is increased, the inner orbitals, HOMO-2 and HOMO-3, are increasingly ionized. The most significant change is that in the strongest field the HOMO-2 orbital has the largest ionization. This is due to partly its complicated nodal structure and to the fact that the time-dependent Kohn-Sham binding energy (not shown) of this orbital decreases the most in the laser field.

According to the enhanced ionization model, as the C-H bond length of the molecule increases there is a

corresponding increase in the ionization rate. To check this Ref. [40] studied the ionization from bond stretched molecular states using the TDHF approach. This model is an approximation since the laser pulse increases the bond length and ionizes the molecule simultaneously. Hence in the stretched configurations the electron number is decreased and these configurations are positively charged. For simplicity this effect was neglected. While our TDDFT simulations with the Ehrenfest dynamics do not suffer from this drawback, it is unclear how important the enhanced ionization effect is to the total ionization. We have therefore repeated the TDDFT calculations without Ehrenfest dynamics, i.e. with ions held fixed in the ground state geometry or in bond stretched geometries.

Fig. 3(a) shows that for low fields the ionization from moving or fixed nuclei are nearly the same. This is not surprising as the ions barely move in the low fields. At  $14 \times 10^{14} \text{ W/cm}^2$ , the two C-H bond lengths increase (asymmetrically) from 1.076 Å to 3.744 Å and to 3.909 Å by the time the ionization completes. The bond stretching causes an additional ionization of 0.9 electrons rel-

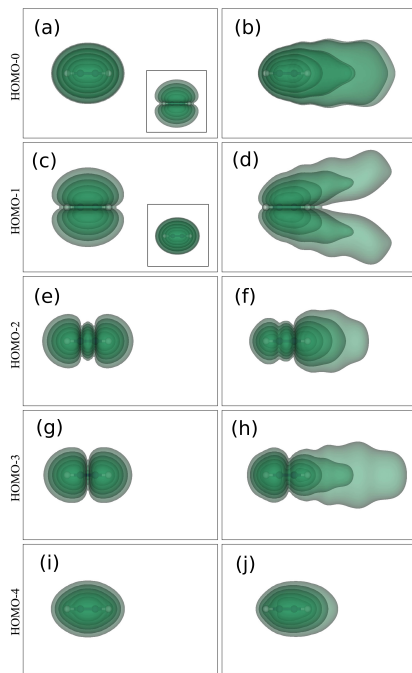


FIG. 4. (Color online) Time evolution of the Kohn-Sham orbitals in acetylene subjected to a 4.5 fs pulse with a peak intensity of  $4 \times 10^{14}$  W/cm<sup>2</sup> and field polarization parallel to the molecular axis. Here we show the absolute squares of the orbitals at  $t = 0$  fs (left column) and at an instant when the laser field magnitude is near its peak at  $t = 11.9$  fs (right column). The insets show the HOMO and HOMO-1 rotated by 90° about the molecular axis. For an animated version see the Supplemental Material [52].

ative to the fixed ions case. This additional ionization comes primarily from the increased ionization of the inner orbitals, HOMO-2 and HOMO-3. When the ion positions are fixed in the ground state geometry ( $R_{C-H} = 1.076$  Å), the ionization of the inner orbitals is suppressed, see Fig. 3(i).

To further investigate the effect of bond stretching on the ionization, we have repeated the fixed ion calculations for several extended geometries. Fig. 3(i) shows that the total ionization increases with the C-H bond lengths in qualitative agreement with Lötstedt et al. [40]. If the ions are fixed in the ground state geometry, the HOMO and HOMO-1 are ionized the most. As the C-H bond length is increased, the HOMO-2 and HOMO-3 become more ionized. At a C-H bond length of  $R = 1.8$  Å the ionization is dominated by the inner orbitals, HOMO-2 and HOMO-3. At the same time the ionization of the HOMO and HOMO-1 is slightly suppressed. The increased ionization of the HOMO-2 and HOMO-3 is partially because they are less tightly bound in the stretched configurations, see Fig. 5(a). The fixed ion model qualitatively matches the orbital dynamics seen with the Ehrenfest dynamics, Fig. 3(a), where the ionization of the HOMO-2 and HOMO-3 overtakes the HOMO and HOMO-1 at

intensities high enough to cause bond stretching. Hence, the enhanced ionization mechanism works primarily by ionizing the inner orbitals.

Finally, we have run calculations with longer pulses to see if Coulomb explosion appears within the Ehrenfest scheme at lower intensities. Table I shows the summary of results for 15 fs and 25 fs pulses over three intensities. The longer pulses increase the ionization, and Coulomb explosion appears at an intensity of  $7 \times 10^{14}$  W/cm<sup>2</sup>. At  $4 \times 10^{14}$  W/cm<sup>2</sup> the probability of bond breaking remains too low for Coulomb explosion to appear in the simulations. At  $14 \times 10^{14}$  W/cm<sup>2</sup> the carbon ions also dissociate. The kinetic energy of the emitted protons is two times larger for the 15 fs pulse than for the 4.5 fs pulse (see Table I), but further increase of the pulse duration does not increase the kinetic energy in this case.

Figs. 3(b) and (c) show the orbital and total ionization versus intensity for pulse durations 15 and 25 fs. At  $4 \times 10^{14}$  W/cm<sup>2</sup>, where bond stretching does not occur, the HOMO and HOMO-1 remain the most ionized orbitals. At the higher intensities the enhanced ionization due to bond stretching greatly increases the ionization of the HOMO-2 and HOMO-3. Once again the ionization of the inner orbitals surpasses that of the HOMO and HOMO-1 and now the effect is much more pronounced.

Fig. 3(a)-(c) show that in our simulations the HOMO-2 and HOMO-3 dominate the ionization in high intensity laser fields with long pulse widths. As we have noted previously, the HOMO-2 and HOMO-3 are less deeply bound in stretched configurations, see Fig. 5(a), and this explains why the HOMO-2 and HOMO-3's ionization increases dramatically with stronger pulses. However, we have not explained why the HOMO-2 and HOMO-3's ionization surpasses the HOMO and HOMO-1. Several recent experiments [19, 53–60] have also observed greater ionization from the inner orbitals. The experiments attribute this finding to (i) the different geometries of the corresponding orbitals with respect to the direction of the laser field and (ii) an increased ionization coming from the tail of the wave function in the direction of the ionization [60].

The energy ordering HOMO, HOMO-1, etc. refer to “global” properties of the orbitals averaged over space. The above arguments suggest that local properties, i.e. how much binding a certain part of the wave function feels, may play an important role. To illustrate this, Fig. 5(b) shows the average density of the ground state orbitals along the alignment axis of the molecule. Although the inner orbitals are more deeply bound, they have an extended weakly bound tail which strongly contributes to the ionization.

This picture is only valid for the ground state—once the laser is turned on ionization starts and the potential and densities change. Nevertheless this picture illustrates the origin of the larger contribution of the inner orbitals.



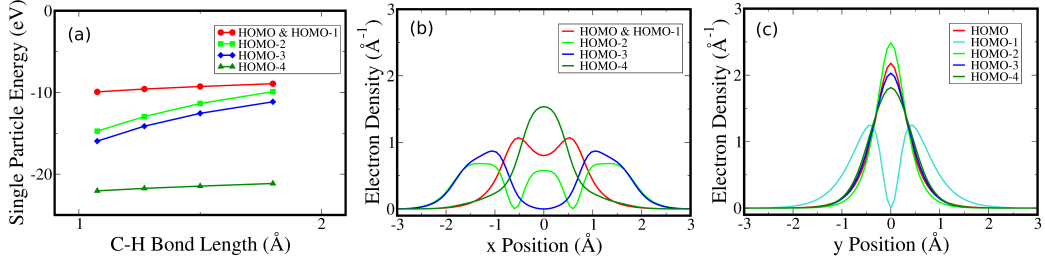


FIG. 5. (Color online) Panel (a) shows the ground state Kohn–Sham single particle energies as a function of C–H bond length. Panel (b) shows the average density of the ground state Kohn–Sham orbitals along the alignment axis of the molecule (x axis). Panel (c) shows the average density of the ground state Kohn–Sham orbitals along an axis perpendicular to the alignment axis of the molecule (y axis). Panels (b) and (c) refer to  $C_2H_2$  in its equilibrium geometry.

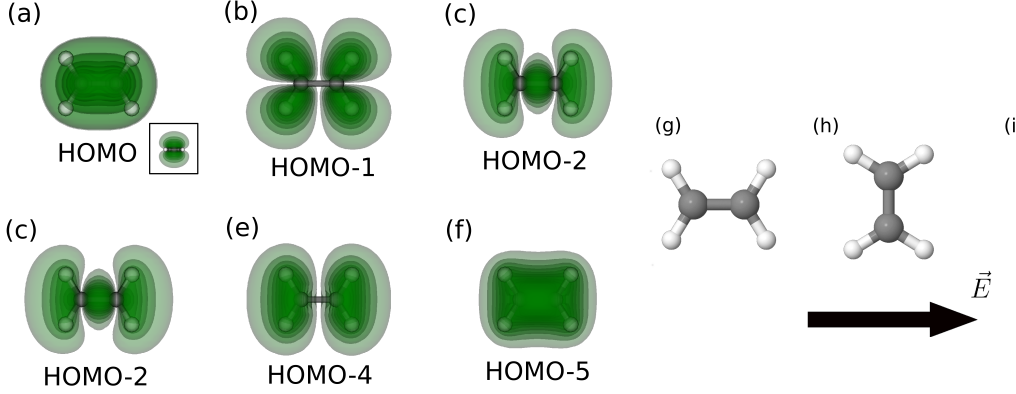


FIG. 6. (Color online) Ground state Kohn–Sham orbitals of ethylene,  $C_2H_4$ . (a) The HOMO with an inset showing a top down view of the HOMO, (b) the HOMO-1, (c) the HOMO-2, (d) the HOMO-3, (e) the HOMO-4, (f) the HOMO-5. Panels (g)–(i) show the three molecular alignments relative to the electric field of the laser that are considered: (g) C–C parallel, (h) C–C bond perpendicular, and (i) all bonds perpendicular to the laser polarization.

## 2. Acetylene in a laser field polarized perpendicularly to the molecular axis

As the angle between the molecule and the laser field is increased to  $22.5^\circ$  and  $45^\circ$ , the kinetic energy of the protons and the total ionization decreases (see Table I). Eventually, the protons only vibrate in the perpendicular direction. With the molecular alignment axis perpendicular to the laser polarization, 4.5 fs pulses did not produce Coulomb explosion in our simulations. Stronger pulses with a duration of 15 fs and 25 fs proved sufficient, though.

A one dimensional projection of the Coulomb explosion in the perpendicular case is shown in Fig. 1(g)–(j). The pulse width is 25 fs and the intensity is  $14 \times 10^{14}$  W/cm<sup>2</sup>. Unlike the parallel case, where the Coulomb explosion was due to the interplay of the laser force on the nuclei, the laser induced oscillation of the electrons, and the ionization, here the fragmentation is only the result of bonds weakened by the ionization. The force exerted on the protons by the perpendicular laser field causes only a

slight oscillation in the motion of the protons perpendicular to the molecular axis. However, the main component of the total force is due to the bond breaking and the protons leave in the up and down directions symmetrically. Fig. 2(d) shows the force on the protons. For Coulomb explosion to occur a stronger and longer pulse is required than in the parallel case, see Figs. 2(a)–(c). However, as seen in the parallel case, the model and Ehrenfest forces are very similar after the peak of the laser field.

We now turn to a more detailed analysis of the ionization dynamics using the the full TDDFT model with Ehrenfest dynamics. Figs. 3(d)–(e) show the total and orbital ionization dynamics. Due to the different symmetry, the ionization of the Kohn–Sham orbitals is quite different in the perpendicular case compared to the parallel one. Consider the short 4.5 fs pulse, Fig. 3(d). The ionization hierarchy of the orbitals from least to greatest is HOMO-4, HOMO-3, HOMO-2, HOMO, and HOMO-1. The two highest levels are no longer degenerate since the symmetry of the orbitals about the polarization axis has been broken. The tail of the HOMO-1 orbital in the direction of the laser polarization extends much further than any of the other orbitals, see Fig. 5(b). Hence, the ionization overwhelmingly comes from the HOMO-1 or-

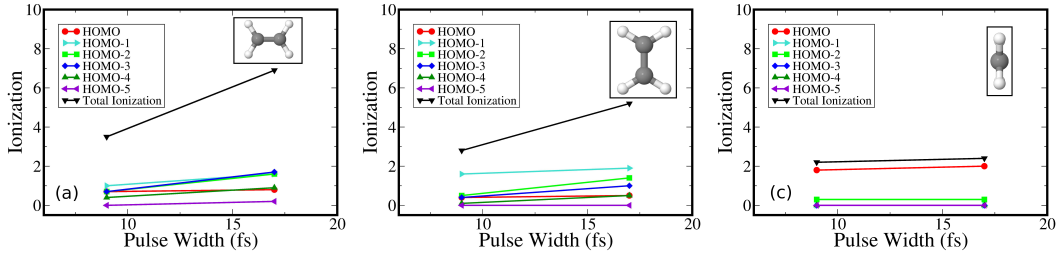


FIG. 7. (Color online) Total and orbital ionization as a function of laser pulse duration for three alignments of  $C_2H_4$ . The laser intensity is fixed at  $8 \times 10^{14} \text{ W/cm}^2$ . C-C bond (a) parallel, (b) perpendicular to the laser polarization direction with the C-H bonds neither parallel nor perpendicular to it. (c) all bonds are perpendicular to the laser polarization direction.

bital and it loses more electrons than any of the orbitals in the parallel case.

Even at  $14 \times 10^{14} \text{ W/cm}^2$  the 4.5 fs pulse does not induce Coulomb explosion. The two C-H bonds stretch symmetrically from  $1.076 \text{ \AA}$  to  $1.553 \text{ \AA}$  by the time that ionization completes. This moderate increase in the bond length leads to a moderate enhanced ionization of 0.1 electrons relative to the case where the ions are fixed in the ground state, see Fig. 3(d). Furthermore, the ionization from the HOMO-2 and HOMO-3 remains small since there is no enhanced ionization.

Pulses with a duration of 15 and 25 fs and a peak intensity of  $14 \times 10^{14} \text{ W/cm}^2$  are now sufficient to cause Coulomb explosion in the simulations. However, the kinetic energy of the emitted protons is about half that of the parallel case (see Table I). The bond stretching leads to an enhanced ionization effect not seen for the 4.5 fs pulses, and there is a substantial increase in the ionization from the HOMO-2, see Figs. 3(e)-(f). While the HOMO-2 surpasses the HOMO, the HOMO-1 remains the dominant source of ionization. Unlike the parallel case, the HOMO-3 plays very little role in the total ionization.

### B. $C_2H_4$

The ionization and molecular dynamics of ethylene,  $C_2H_4$ , has been studied by varying the duration of the laser pulses, see Table I. The two laser pulses that we used exhibit an intensity and duration typical in experiments [31]. Three simple geometric alignments were considered, see Fig. 6(g)-(i).

We briefly describe the ions' dynamics observed in our simulations, see Table I. For the geometry with all bonds perpendicular to the laser polarization [Fig. 6(i)], the C-H bonds remain essentially unchanged and the C-C bond stretches but dissociation does not occur. For the geometry with only the C-C bond perpendicular to the laser polarization [Fig. 6(h)], the C-H bonds break slowly for the 9 fs pulse. At 17 fs the C-H bonds dissociate much more quickly due to the increased ionization. The C-C

bond remains nearly unchanged for both pulses. For the geometry with the C-C bond parallel to the laser polarization [Fig. 6(g)], all of the C-H bonds fragment via a Coulomb explosion for both pulse durations. At the longer pulse duration of 17 fs the C-C bond also fragments.

We now turn to the orbital ionization dynamics. Fig. 7 shows the occupation number of the time-dependent Kohn-Sham orbitals for the three geometries and the two laser pulses. When all bonds are oriented perpendicularly to the laser field [Fig. 6(i)], the HOMO nearly completely ionizes. The HOMO-2 is the next most ionized, losing nearly 0.5 electrons. The other orbitals stay unionized. Increasing the duration of the laser pulse has little effect on the orbital and total ionization.

We next consider the geometry where only the C-C bond is oriented perpendicular to the laser field [Fig. 6(h)]. The orbital ionization dynamics are dramatically different from the previous case. The HOMO-1 is now the dominant source of ionization. At 9 fs the HOMO, HOMO-2, and HOMO-3 each lose nearly 0.5 electrons while the HOMO-4 and HOMO-5 are barely ionized. At 17 fs the C-H bonds stretch more quickly causing a more pronounced enhanced ionization effect. Owing to both the direct effect of the increased pulse width and the enhanced ionization effect, the total ionization in the 17 fs pulse is increased by about 2 electrons. Furthermore, the inner orbitals HOMO-2, HOMO-3, and HOMO-4 are much more ionized, losing about 1.5, 1, and 0.5 electrons, respectively. The ionization dynamics from the HOMO and HOMO-1 remain essentially unchanged by the increased pulse duration. The HOMO-5 is unionized in either pulse.

Finally, we consider the geometry in Fig. 6(g). At a pulse duration of 9 fs the HOMO-1 is again the most ionized orbital, losing nearly one electron. The HOMO, HOMO-2, and HOMO-4 lose nearly 0.75 electrons each. The HOMO-4 loses somewhat less than 0.5 electrons, and the HOMO-5 stays unionized. For the 17 fs pulse, the total ionization is increased by both the direct effect of the longer pulse duration and a more prominent enhanced ionization effect. The enhanced ionization effect is increased since the bonds stretch at a much faster rate in the longer pulse. Hence, the molecule reaches a stretched



	KE (eV)	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	HOMO-5	Num. Electrons
C <sub>2</sub> H <sub>2</sub> , parallel								
$4 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.7	1.7	1.9	1.9	2.0	X	9.1
$7 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.5	1.5	1.7	1.7	2.0	X	8.3
$14 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	11.7	1.2	1.2	1.1	1.2	1.9	X	6.6
$4 \times 10^{14}$ W/cm <sup>2</sup> , 15 fs	0	1.5	1.5	1.8	1.6	2.0	X	8.5
$7 \times 10^{14}$ W/cm <sup>2</sup> , 15 fs	14.9	1.3	1.3	0.3	0.5	1.9	X	5.3
$14 \times 10^{14}$ W/cm <sup>2</sup> , 15 fs	22.8	1.1	1.1	0.6	0.2	1.6	X	4.6
$4 \times 10^{14}$ W/cm <sup>2</sup> , 25 fs	0	1.5	1.5	1.7	1.5	2.0	X	8.1
$7 \times 10^{14}$ W/cm <sup>2</sup> , 25 fs	16.5	1.3	1.3	0.7	0.2	1.9	X	5.4
$14 \times 10^{14}$ W/cm <sup>2</sup> , 25 fs	22.5	0.9	0.9	0.5	0.1	1.4	X	3.6
C <sub>2</sub> H <sub>2</sub> , 22.5°								
$4 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.7	1.5	1.9	1.9	2.0	X	9.0
$7 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.6	1.3	1.8	1.8	2.0	X	8.4
$14 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	8.5	1.3	1.0	1.4	1.4	1.9	X	7.0
C <sub>2</sub> H <sub>2</sub> , 45°								
$4 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.8	1.3	2.0	2.0	2.0	X	9.0
$7 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.7	1.0	1.9	1.9	2.0	X	8.4
$14 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	4.9	1.5	0.7	1.7	1.5	2.0	X	7.3
C <sub>2</sub> H <sub>2</sub> , perpendicular								
$4 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.9	1.1	2.0	2.0	2.0	X	9.0
$7 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.8	0.8	1.9	2.0	2.0	X	8.5
$14 \times 10^{14}$ W/cm <sup>2</sup> , 4.5 fs	0	1.6	0.4	1.7	1.9	2.0	X	7.6
$4 \times 10^{14}$ W/cm <sup>2</sup> , 15 fs	0	1.9	0.7	2.0	2.0	2.0	X	8.6
$7 \times 10^{14}$ W/cm <sup>2</sup> , 15 fs	0	1.7	0.3	1.9	2.0	2.0	X	8.0
$14 \times 10^{14}$ W/cm <sup>2</sup> , 15 fs	10.0	1.4	0.0	0.9	1.9	2.0	X	6.3
$4 \times 10^{14}$ W/cm <sup>2</sup> , 25 fs	0	1.9	0.6	2.0	2.0	2.0	X	8.4
$7 \times 10^{14}$ W/cm <sup>2</sup> , 25 fs	0	1.7	0.2	1.9	2.0	2.0	X	7.8
$14 \times 10^{14}$ W/cm <sup>2</sup> , 25 fs	13.7	1.4	0.0	0.4	1.9	2.0	X	5.7
C <sub>2</sub> H <sub>4</sub> , C-C parallel								
$8 \times 10^{14}$ W/cm <sup>2</sup> , 9 fs	5.9	1.3	1.0	1.3	1.3	1.6	2.0	8.5
$8 \times 10^{14}$ W/cm <sup>2</sup> , 17 fs	18.8	1.2	0.4	0.4	0.3	1.1	1.8	5.1
C <sub>2</sub> H <sub>4</sub> , C-C perpendicular								
$8 \times 10^{14}$ W/cm <sup>2</sup> , 9 fs	0.2	1.6	0.6	1.5	1.6	1.9	2.0	9.2
$8 \times 10^{14}$ W/cm <sup>2</sup> , 17 fs	9.6	1.5	0.1	0.6	1.0	1.5	2.0	6.8
C <sub>2</sub> H <sub>4</sub> , perpendicular								
$8 \times 10^{14}$ W/cm <sup>2</sup> , 9 fs	0	0.2	2.0	1.7	2.0	2.0	2.0	9.8
$8 \times 10^{14}$ W/cm <sup>2</sup> , 17 fs	0	0.0	2.0	1.7	2.0	2.0	2.0	9.6

TABLE I. Orbital ionization dynamics of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> for various laser pulses and molecular alignments. The first column gives the kinetic energy of the hydrogen ions (per ion). The subsequent columns show the occupation number of each Kohn–Sham orbital and the total electron number at the end of the simulation. C<sub>2</sub>H<sub>2</sub> has only five occupied orbitals (HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4), and hence the column for the occupation of the HOMO-5 has been marked with an X to indicate that it is not applicable in this case.

configuration ( $R \geq R_c$ ) earlier in the ionization process. Furthermore, the ionization of all orbitals except for the HOMO has increased. The HOMO-1, HOMO-2, and HOMO-3 are now nearly completely emptied. The ionization of the HOMO-4 has overtaken the ionization from the HOMO. The ionization from the HOMO-5 increases

to nearly 0.25 electrons.

#### IV. SUMMARY

In summary, we have studied the ionization dynamics of acetylene, C<sub>2</sub>H<sub>2</sub>, and ethylene, C<sub>2</sub>H<sub>4</sub>, in strong

laser pulses with various durations and peak intensities for different molecular alignments relative to the linear laser polarization direction using the TDDFT method. It is found that the molecular alignment has a dramatic effect on the total ionization. We have observed that bond stretching and bond breaking leads to an increase of the ionization efficiency, i.e. enhanced ionization, in qualitative agreement with previous theoretical investigations [38–40]. We have also calculated the ionization from individual Kohn-Sham orbitals. It was shown that the enhanced ionization mechanism primarily affects the inner valence orbitals. That is, the inner orbitals are more ionized when bond stretching occurs since they are more weakly bound in the stretched configurations. For some alignments and laser pulse parameters the ionization of the inner orbitals is greater than the highest occupied molecular orbital, owing to ionization from their

extended weakly bound tails. Topics for future work include an investigation of larger polyatomic molecules and the effects of circular polarization. Future experiments planned on aligned molecules with short strong laser pulses will be able to test the predictions of this paper and will stimulate further analysis.

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- [1] B. Manschwetus, T. Nubbemeyer, K. Gorling, G. Steinmeyer, U. Eichmann, H. Rottke, and W. Sandner, *Phys. Rev. Lett.* **102**, 113002 (2009).
  - [2] P. von den Hoff, I. Znakovskaya, M. F. Kling, and R. de Vivie-Riedle, *Chem. Phys.* **366**, 139 (2009).
  - [3] G. Sansone, F. Kelkensberg, J. F. Perez-Torres, F. Morales, M. F. Kling, W. Siu, O. Ghafur, P. Johnsson, M. Swoboda, E. Benedetti, F. Ferrari, F. Lepine, J. L. Sanz-Vicario, S. Zherebtsov, I. Znakovskaya, A. L’Huillier, M. Y. Ivanov, M. Nisoli, F. Martin, and M. J. J. Vrakking, *Nature (London)* **465**, 763 (2010).
  - [4] I. Bocharova, R. Karimi, E. F. Penka, J.-P. Brichta, P. Lassonde, X. Fu, J.-C. Kieffer, A. D. Bandrauk, I. Litvinyuk, J. Sanderson, and F. Légaré, *Phys. Rev. Lett.* **107**, 063201 (2011).
  - [5] X. Gong, Q. Song, Q. Ji, H. Pan, J. Ding, J. Wu, and H. Zeng, *Phys. Rev. Lett.* **112**, 243001 (2014).
  - [6] F. Krausz and M. Ivanov, *Rev. Mod. Phys.* **81**, 163 (2009).
  - [7] Y. Liu, X. Liu, Y. Deng, C. Wu, H. Jiang, and Q. Gong, *Phys. Rev. Lett.* **106**, 073004 (2011).
  - [8] X. Xie, K. Doblhoff-Dier, S. Roither, M. S. Schöffler, D. Kartashov, H. Xu, T. Rathje, G. G. Paulus, A. Baltuška, S. Gräfe, and M. Kitzler, *Phys. Rev. Lett.* **109**, 243001 (2012).
  - [9] X. Xie, K. Doblhoff-Dier, H. Xu, S. Roither, M. S. Schöffler, D. Kartashov, S. Erattupuzha, T. Rathje, G. G. Paulus, K. Yamanouchi, A. Baltuška, S. Gräfe, and M. Kitzler, *Phys. Rev. Lett.* **112**, 163003 (2014).
  - [10] X. Xie, S. Roither, M. Schöffler, E. Lötstedt, D. Kartashov, L. Zhang, G. G. Paulus, A. Iwasaki, A. Baltuška, K. Yamanouchi, and M. Kitzler, *Phys. Rev. X* **4**, 021005 (2014).
  - [11] V. Kumarappan, L. Holmegaard, C. Martiny, C. B. Madsen, T. K. Kjeldsen, S. S. Viftrup, L. B. Madsen, and H. Stapelfeldt, *Phys. Rev. Lett.* **100**, 093006 (2008).
  - [12] L. Holmegaard, J. H. Nielsen, I. Nevo, H. Stapelfeldt, F. Filsinger, J. Küpper, and G. Meijer, *Phys. Rev. Lett.* **102**, 023001 (2009).
  - [13] L. Holmegaard, J. L. Hansen, L. Kalhøj, S. L. Kragh, H. Stapelfeldt, F. Filsinger, J. Küpper, G. M. D. Dimitrovski, M. Abu-samha, C. P. J. Martiny, and L. B. Madsen, *Nature Phys.* **6**, 428 (2010).
  - [14] C. Z. Bisgaard, O. J. Clarkin, G. Wu, A. M. D. Lee, O. Geßner, C. C. Hayden, and A. Stolow, *Science* **323**, 1464 (2009).
  - [15] M. Meckel, D. Comtois, D. Zeidler, A. Staudte, D. Pavičić, H. C. Bandulet, H. Pépin, J. C. Kieffer, R. Dörner, D. M. Villeneuve, and P. B. Corkum, *Science* **320**, 1478 (2008).
  - [16] S. Bubin, M. Atkinson, K. Varga, X. Xie, S. Roither, D. Kartashov, A. Baltuška, and M. Kitzler, *Phys. Rev. A* **86**, 043407 (2012).
  - [17] A. Talebpour, A. Bandrauk, J. Yang, and S. Chin, *Chemical Physics Letters* **313**, 789 (1999).
  - [18] B. K. McFarland, J. P. Farrell, P. H. Bucksbaum, and M. Gühr, *Science (New York, N.Y.)* **322**, 1232 (2008).
  - [19] H. Akagi, T. Otobe, A. Staudte, A. Shiner, F. Turner, R. Dörner, D. M. Villeneuve, and P. B. Corkum, *Science* **325**, 1364 (2009).
  - [20] P. Hoff, I. Znakovskaya, S. Zherebtsov, M. F. Kling, and R. Vivie-Riedle, *Applied Physics B* **98**, 659 (2009).
  - [21] Z. Wu, C. Wu, X. Liu, Y. Deng, Q. Gong, D. Song, and H. Su, *The journal of physical chemistry. A* **114**, 6751 (2010).
  - [22] A. E. Boguslavskiy, J. Mikosch, A. Gijsbertsen, M. Spanner, S. Patchkovskii, N. Gador, M. J. J. Vrakking, and A. Stolow, *Science (New York, N.Y.)* **335**, 1336 (2012).
  - [23] J. Wu, L. Schmidt, M. Kunitski, M. Meckel, S. Voss, H. Sann, H. Kim, T. Jahnke, A. Czasch, and R. Dörner, *Physical Review Letters* **108**, 183001 (2012).
  - [24] C. Wu, H. Zhang, H. Yang, Q. Gong, D. Song, and H. Su, *Physical Review A* **83**, 033410 (2011).
  - [25] J. Mikosch, A. E. Boguslavskiy, I. Wilkinson, M. Spanner, S. Patchkovskii, and A. Stolow, *Physical Review Letters* **110**, 023004 (2013).

- [26] S. Weber, M. Oppermann, M. Ivanov, and J. Marangos, *Journal of Modern Optics* **60**, 1379 (2013).
- [27] T. Seideman, M. Y. Ivanov, and P. B. Corkum, *Physical Review Letters* **75**, 2819 (1995).
- [28] T. Zuo and A. D. Bandrauk, *Phys. Rev. A* **52**, R2511 (1995).
- [29] D. M. Villeneuve, M. Y. Ivanov, and P. B. Corkum, *Phys. Rev. A* **54**, 736 (1996).
- [30] S. Roither, X. Xie, D. Kartashov, L. Zhang, M. Schöffler, H. Xu, A. Iwasaki, T. Okino, K. Yamanouchi, A. Baltuska, and M. Kitzler, *Phys. Rev. Lett.* **106**, 163001 (2011).
- [31] X. Xie, S. Roither, M. Schöffler, H. Xu, S. Bubin, E. Lötstedt, S. Erattuphuza, A. Iwasaki, D. Kartashov, K. Varga, G. G. Paulus, A. Baltuska, K. Yamanouchi, and M. Kitzler, *Phys. Rev. A* **89**, 023429 (2014).
- [32] E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).
- [33] P. Ehrenfest, *Z. Phys.* **45**, 455 (1927).
- [34] M. V. Ammosov, N. B. Delone, and V. P. Krainov, *Sov. Phys. JETP* **64**, 1191 (1986).
- [35] X. M. Tong, Z. X. Zhao, and C. D. Lin, *Phys. Rev. A* **66**, 033402 (2002).
- [36] K. Codling, L. J. Frasinski, and P. A. Hatherly, *J. Phys. B* **22**, L321 (1989).
- [37] D. Dimitrovski, C. P. J. Martiny, and L. B. Madsen, *Phys. Rev. A* **82**, 053404 (2010).
- [38] E. Lötstedt, T. Kato, and K. Yamanouchi, *Phys. Rev. A* **85**, 041402 (2012).
- [39] E. Lötstedt, T. Kato, and K. Yamanouchi, *Phys. Rev. A* **86**, 023401 (2012).
- [40] E. Lötstedt, T. Kato, and K. Yamanouchi, *J. Chem. Phys.* **138**, 104304 (2013).
- [41] E. Livshits and R. Baer, *J. Phys. Chem. A* **110**, 8443 (2006).
- [42] M. Isla and J. A. Alonso, *J. Phys. Chem. C* **111**, 17765 (2007).
- [43] M.-P. Gaigeot, P. Lopez-Tarifa, F. Martin, M. Alcamí, R. Vuilleumier, I. Tavernelli, M.-A. H. du Penhoat, and M.-F. Politis, *Mutat. Res. Rev. Mutat. Res.* **704**, 45 (2010), eSF-EMBO Conference: Spatio-Temporal Radiation Biology: Transdisciplinary Advances for Biomedical Applications.
- [44] A. Debnarova, S. Techert, and S. Schmatz, *Phys. Chem. Chem. Phys.* **14**, 9606 (2012).
- [45] Y. Kawashita, T. Nakatsukasa, and K. Yabana, *J. Phys. Condens. Matter* **21**, 064222 (2009).
- [46] J. Haruyama, C. Hu, and K. Watanabe, *Phys. Rev. A* **85**, 062511 (2012).
- [47] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [48] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [49] A. Castro, M. A. L. Marques, and A. Rubio, *The Journal of Chemical Physics* **121**, 3425 (2004).
- [50] D. E. Manolopoulos, *J. Chem. Phys.* **117**, 9552 (2002).
- [51] P. J. Linstrom and W. G. Mallard, eds., *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (National Institute of Standards and Technology, Gaithersburg MD, 20899, 2001).
- [52] See Supplemental Material at <http://journal.web.site/path> for an animation of the time evolution of the Kohn-Sham orbitals.
- [53] I. V. Litvinyuk, F. Légaré, P. W. Dooley, D. M. Villeneuve, P. B. Corkum, J. . Zanghellini, A. Pegarkov, C. Fabian, and T. Brabec, *Phys. Rev. Lett.* **94**, 033003 (2005).
- [54] W. A. Bryan, S. L. Stebbings, J. McKenna, E. M. L. English, M. Suresh, J. Wood, B. Srigengan, I. C. E. Turcu, J. M. Smith, E. J. Divall, C. J. Hooker, A. J. Langley, J. L. Collier, I. D. Williams, and W. R. Newell, *Nature Physics* **2**, 379 (2006).
- [55] T. Kanai, S. Minemoto, and H. Sakai, *Nature* **435**, 470 (2005).
- [56] W. Li, X. Zhou, R. Lock, S. Patchkovskii, A. Stolow, H. C. Kapteyn, and M. M. Murnane, *Science* **322**, 1207 (2008).
- [57] X. Zhou, R. Lock, W. Li, N. Wagner, M. M. Murnane, and H. C. Kapteyn, *Phys. Rev. Lett.* **100**, 073902 (2008).
- [58] W. Boutu, S. Haessler, H. Merdji, P. Breger, G. Waters, M. Stankiewicz, L. J. Frasinski, R. Taieb, J. Caillat, A. Maquet, P. Monchicourt, B. Carre, and P. Salieres, *Nature Physics* **4**, 545 (2008).
- [59] B. K. McFarland, J. P. Farrell, P. H. Bucksbaum, and M. Ghr, *Science* **322**, 1232 (2008), <http://www.sciencemag.org/content/322/5905/1232.full.pdf>.
- [60] O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villeneuve, P. Corkum, and M. Y. Ivanov, *Nature* **460**, 972 (2009).