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Fragmentation in Coulomb explosion of hydrocarbon molecules

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Fragmentation dynamics in the Coulomb explosion of hydrocarbons, specifically methane, ethane, propane, and butane, are investigated using time dependent density functional theory (TDDFT) simulations. The goal of this work is to elucidate the distribution of fragments generated under laser-driven Coulomb explosion conditions. Detailed analysis reveals the types of fragments formed, their respective charge states, and the optimal laser intensities required for achieving various fragmentations. Our results indicate distinct fragmentation patterns for each hydrocarbon, correlating with the molecular structure and ionization potential. Additionally, we identify the laser parameters that maximize fragmentation efficiency, providing valuable insights for experimental setups. This research advances our understanding of Coulomb explosion mechanisms and offers a foundation for further studies in controlled molecular fragmentation.

I. INTRODUCTION

Coulomb explosion, a process where molecules undergo rapid ionization resulting in repulsive interactions between charged fragments, has garnered significant attention due to its relevance across various scientific and technological domains. The advent of ultra-intense femtosecond lasers has made it possible to probe this phenomenon with high temporal resolution, making it a key subject of both theoretical and experimental investigations. Applications of Coulomb explosion span molecular imaging [1–26], structural dynamics [27–38], generation of bright keV x-ray photons [39, 40], and production of highly energetic electrons [41]. In addition, fragment formation during Coulomb explosion has been extensively studied [36, 42–53].

Hydrocarbon molecules, particularly methane, ethane, propane, and butane, have been used as precursors in numerous Coulomb explosion experiments [46, 54–58]. These studies have reported key observations such as the kinetic energies of ejected protons, emission spectra from the resulting plasma, and fragment yields over a range of pulse intensities. However, a comprehensive dynamical description of the fragmentation process is often missing—there has been limited focus on identifying the optimal laser pulse parameters and intensities that maximize fragmentation efficiency for the first four alkanes in the series.

Previous theoretical efforts to model Coulomb explosions include classical models, which neglect quantum effects [3, 5, 59], semiclassical methods [11, 60], and *ab initio* approaches [61–72]. Classical models often assume purely repulsive forces between positively charged atomic cores, lacking the attractive forces from electron densities that could form bonds and define molecular fragments.

In contrast, *ab initio* methods, such as TDDFT [73, 74], capture these electron interactions, allowing for the formation of bonded fragments that classical models cannot represent. Given TDDFT’s proven accuracy in reproducing experimental results [62, 64–67], we have selected this approach for our study.

In this work, we employ TDDFT simulations to comprehensively examine the fragmentation dynamics of hydrocarbons under Coulomb explosion induced by intense laser fields. This study is motivated by recent experiments that observed CH radicals and other fragments resulting from the Coulomb explosion of ethene [75] and butane [76]. The results are somewhat surprising, as earlier experiments [29, 67] primarily demonstrated that strong laser pulses predominantly stripped protons from hydrocarbon molecules via a CH bond stretching mechanism. We will analyze the nature and charge distributions of the resulting fragments, as well as the electron dynamics during ionization and the post-ionization molecular motion. Furthermore, we will identify the laser intensities that yield optimal fragmentation, providing critical insights for designing experiments.

Our focus on methane, ethane, propane, and butane allows us to uncover distinct fragmentation behaviors linked to the molecular structure and ionization potentials of these hydrocarbons. By pinpointing the laser parameters that maximize fragmentation efficiency, this study enhances the understanding of Coulomb explosion mechanisms and lays the groundwork for future investigations into controlled molecular fragmentation.

II. COMPUTATIONAL METHOD

The simulations were performed using TDDFT for modeling the electron dynamics on a real-space grid with real-time propagation [77], with the Kohn-Sham (KS)

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Hamiltonian of the following form

$$\hat{H}_{\text{KS}}(t) = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ion}}(\mathbf{r}, t) + V_{\text{H}}[\rho](\mathbf{r}, t) + V_{\text{XC}}[\rho](\mathbf{r}, t) + V_{\text{laser}}(\mathbf{r}, t). \quad (1)$$

Here, ρ is the electron density which is defined as the density sum over all occupied orbitals:

$$\rho(\mathbf{r}, t) = \sum_{k=1}^{N_{\text{orbitals}}} 2|\psi_k(\mathbf{r}, t)|^2, \quad (2)$$

where the coefficient 2 accounts for there being two electrons in each orbital (via spin degeneracy) and k is a quantum number labeling each orbital.

V_{ion} in Eq. (1) is the external potential due to the ions, represented by employing norm-conserving pseudopotentials centered at each ion as given by Troullier and Martins [78]. V_{H} is the Hartree potential, defined as

$$V_{\text{H}}(\mathbf{r}, t) = \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (3)$$

and accounts for the electrostatic Coulomb interactions between electrons. The term V_{XC} is the exchange-correlation potential, which is approximated by the adiabatic local-density approximation (ALDA), obtained from a parameterization to a homogeneous electron gas by Perdew and Zunger [79]. The last term in Eq. (1), V_{laser} is the time-dependent potential due to the electric field of the laser, and is described using the dipole approximation, $V_{\text{laser}} = \mathbf{r} \cdot \mathbf{E}_{\text{laser}}(t)$. The electric field $\mathbf{E}_{\text{laser}}(t)$ is given by

$$\mathbf{E}_{\text{laser}}(t) = E_{\text{max}} \exp\left[-\frac{(t-t_0)^2}{2a^2}\right] \sin(\omega t) \hat{\mathbf{k}}, \quad (4)$$

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

At the beginning of the TDDFT calculations, the ground state of the system is prepared by performing a Density-Functional Theory (DFT) calculation. With these initial conditions in place, we then proceed to propagate the Kohn-Sham orbitals, $\psi_k(\mathbf{r}, t)$ over time by using the time-dependent KS equation, given as

$$i\frac{\partial\psi_k(\mathbf{r}, t)}{\partial t} = \hat{H}\psi_k(\mathbf{r}, t). \quad (5)$$

Eq. (5) was solved using the following time propagator

$$\psi_k(\mathbf{r}, t + \delta t) = \exp\left(-\frac{i\hat{H}_{\text{KS}}(t)\delta t}{\hbar}\right) \psi_k(\mathbf{r}, t). \quad (6)$$

This operator is approximated using a fourth-degree Taylor expansion, given as

$$\psi_k(\mathbf{r}, t + \delta t) \approx \sum_{n=0}^4 \frac{1}{n!} \left(\frac{-i\delta t}{\hbar} \hat{H}_{\text{KS}}(t)\right)^n \psi_k(\mathbf{r}, t). \quad (7)$$

The operator is applied for N time steps until the final time, $t_{\text{final}} = N \cdot \delta t$, is obtained. A time step of $\delta t = 1$ as was used in the simulations.

In real-space TDDFT, the Kohn-Sham orbitals are represented at discrete points in real space. These points are organized on a uniform rectangular grid. The accuracy of the simulations is determined by the grid spacing, which is the key parameter that can be adjusted. In our simulations, we used a grid spacing of 0.3 Å and placed 100 points along each of the x , y , and z axes.

To enforce boundary conditions, we set the Kohn-Sham orbitals to zero at the edges of the simulation cell. However, when a strong laser field is applied, ionization can occur, potentially causing unphysical reflections of the wavefunction at the cell boundaries. To address this issue, we implemented a complex absorbing potential (CAP) to dampen the wavefunction as it reaches the boundaries. The specific form of the CAP used in our simulations, as described by Manopolous [80], is given by:

$$-iw(x) = -i\frac{\hbar^2}{2m} \left(\frac{2\pi}{\Delta x}\right)^2 f(y), \quad (8)$$

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

$$f(y) = \frac{4}{c^2} \left(\frac{1}{(1+y)^2} + \frac{1}{(1-y)^2} - 2\right), \quad y = \frac{x-x_1}{\Delta x}. \quad (9)$$

As the molecule is ionized by the laser field, the electron density is directed towards the CAP. Additionally, the ejected fragments carry their electron density move towards the CAP. When any electron density into contact with the CAP, it is absorbed. Consequently, the total electron number

$$N(t) = \int_V \rho(\mathbf{r}, t) d^3x, \quad (10)$$

where V is the volume of the simulation box, will diverge from the initial electron number, $N(0)$. We interpret $N(0) - N(t)$ as the total number of electrons ejected from the simulation box.

Motion of the ions in the simulations were treated classically. Using the Ehrenfest theorem, the quantum forces on the ions 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, giving

$$M_i \frac{d^2 \mathbf{R}_i}{dt^2} = Z_i \mathbf{E}_{\text{laser}}(t) + \sum_{j \neq i}^{N_{\text{ions}}} \frac{Z_i Z_j (\mathbf{R}_i - \mathbf{R}_j)}{|\mathbf{R}_i - \mathbf{R}_j|^3} - \nabla_{\mathbf{R}_i} \int V_{\text{ion}}(\mathbf{r}, \mathbf{R}_i) \rho(\mathbf{r}, t) d\mathbf{r}, \quad (11)$$

where M_i , Z_i , and \mathbf{R}_i are the mass, pseudocharge (valence), and position of the i -th ion, respectively, and N_{ions}

is the total number of ions. This differential equation was time propagated using the Verlet algorithm at every time step δt . This approach has been successfully used to describe the Coulomb explosion of molecules [62, 64–67].

In each simulation, the ion velocities are initialized using a Boltzmann distribution corresponding to 300 K. In typical Coulomb explosion experiments, molecules are introduced into the chamber via a cold molecular beam, and the intense laser field rapidly heats them to high temperatures. Since the molecular temperature changes dynamically during the process, initializing the velocities at 300 K serves as a practical approach to facilitate the exploration of diverse fragmentation pathways. If the ion velocities were held constant, the simulations would yield identical fragmentation outcomes, thus constraining the statistical variability of the results. To ensure a comprehensive distribution of data, more than 50 simulations were conducted for each molecule, allowing for the formation of C_nH_m fragments in several instances across all tested molecules. Due to limited computational resources, no further simulations were performed.

Each molecule in the simulations was positioned at the center of the simulation box, with its longest molecular axis aligned along the x -axis and its shortest axis oriented along the z -axis. In every simulation, the electric field was polarized along the x -axis to maximize ionization [62]. In experimental settings, this precise molecular alignment can be achieved depending on the alignment scheme and the molecule’s polarizability [2].

In the following section, we present the results from a substantial number of simulations conducted on the first four alkanes: methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}), using a laser intensity determined to optimize fragmentation. The laser parameters, including wavelength and duration, were modeled after the pulse described in [76], which follows the functional form outlined in Eq. (4). Thus, for all simulations, the wavelength was set to 890 nm, and the laser pulse duration was set to 7.8 fs (FWHM). The only varying parameter in our simulations was the laser intensity, which was adjusted to explore the ionization, fragmentation, and dissociation ranges for the selected alkanes.

A. Methane (CH_4)

The electron densities and molecular dynamics of a CH_4 molecule during a Coulomb explosion simulation are illustrated in Fig. 1. These snapshots are from one of the 71 simulations conducted using CH_4 as the precursor molecule. Initially, the snapshots show how the laser field rips the electron density away from the molecule, triggering rapid ionization. As shown in the figure, significant ionization begins when the electric field magnitude reaches approximately 5.5 V/\AA at 14 fs. The ionization process concludes when the laser field falls below 6 V/\AA at around 24 fs, leaving the molecule with 5.3 valence electrons. This near-triple ionization creates

strong Coulomb repulsion between the resulting fragments, causing them to separate rapidly.

In our calculations, the electron density is integrated over a finite volume, resulting in non-integer electron counts. Non-integral electron numbers are well-known artifacts of local and semi-local approximations in TDDFT (such as the ALDA functional), where the exact exchange-correlation (xc) potential is approximated. Exact xc potentials, unlike local or semi-local approximations, contain steps and discontinuities that enforce integer electron preferences during molecular dissociation. When these discontinuities are absent, as in ALDA, discretization of the wavefunction can lead to fractions of electrons being ejected, especially under ionization dynamics [62, 64–67].

This phenomenon can be interpreted in several ways. One explanation is that approximately 5.3 electrons remain localized within the molecular region during the simulation, with the fractional charge either recombining with the ionized electron cloud or dissociating over a longer simulation period. Alternatively, a more practical interpretation is that the non-integer charge represents an average: some molecular fragments may retain 5 valence electrons while others retain 6, and 5.3 reflects the mean electron count per fragment. For example, if a hydrogen atom were ejected with a charge of 0.6^+ , it would imply that 60% of the time it is detected as a 1^+ ion and 40% as a neutral hydrogen atom.

The ejected hydrogen fragments are observed moving toward the CAP, where their electrons are absorbed, leading to a further (artificial) reduction in the number of electrons. After the ionization, the remaining fragment (CH_2) undergoes structural rearrangement. Fig. 1 depicts the CH_2 fragment transitioning from a right-bent geometry at 70 fs to a linear conformation at 103 fs, and finally to a left-bent structure at 120 fs. The laser pulse

Alkane	Ionization threshold (W/cm^2)	Fragmentation threshold (W/cm^2)	Dissociation threshold (W/cm^2)
CH_4	7.0×10^{14}	1.1×10^{15}	1.5×10^{15}
C_2H_6	6.1×10^{14}	9.0×10^{14}	1.5×10^{15}
C_3H_8	3.8×10^{14}	7.0×10^{14}	1.5×10^{15}
C_4H_{10}	4.5×10^{14}	7.0×10^{14}	1.3×10^{15}

TABLE I: Approximate pulse intensities required for ionization, fragmentation, and dissociation of the first four alkanes are presented, with a pulse wavelength of 890 nm and a duration of 7.8 fs (FWHM). Pulse intensities below the ionization threshold result in minimal or no dissociation of the molecular structure. Intensities near the fragmentation threshold cause partial molecular breakup, leading to the formation of smaller ionized fragments. Intensities above the dissociation threshold result in nearly complete molecular disintegration, with all atoms being ejected from the molecule.

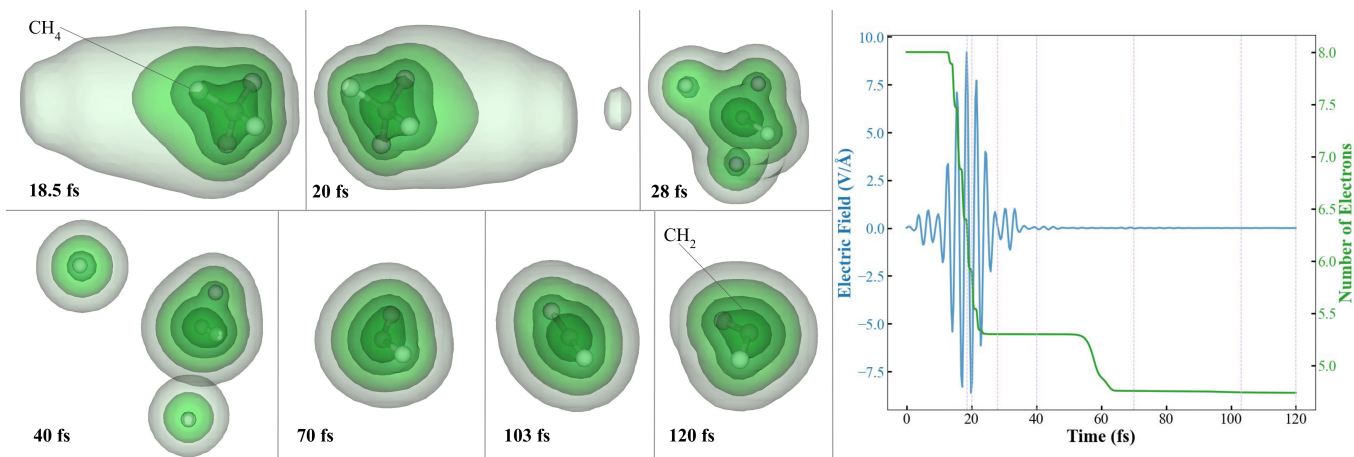


FIG. 1: CH₄ Coulomb explosion snapshots resulting in the formation of one CH₂ molecule and two discharged H atoms have 1.26⁺, 0.62⁺, and 0.84⁺ charges, respectively (the 0.5, 0.1, 0.01, and 0.001 density isosurfaces are displayed). The pulse electric field and the number of electrons in the simulation are shown, with vertical dashed purple lines indicating the specific times in the simulation when each snapshot was captured.

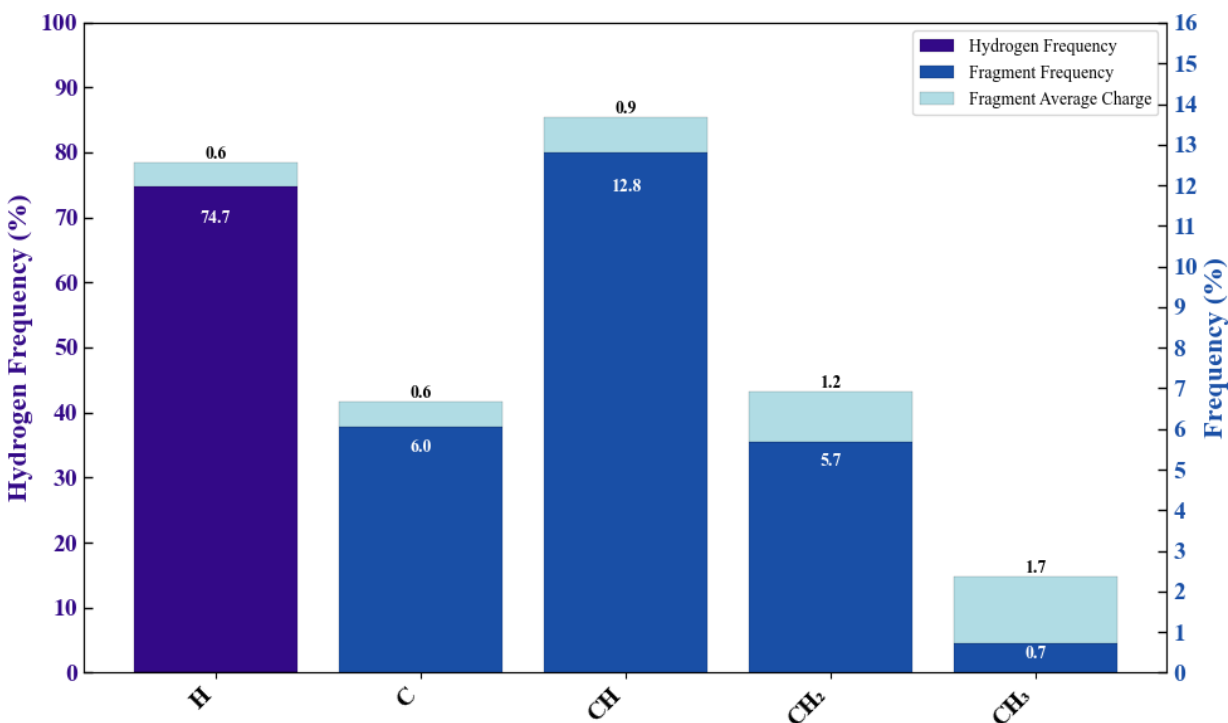


FIG. 2: Average production frequency of each fragment generated in 71 CH₄ Coulomb explosion simulations. The darker columns represent the formation frequency of hydrogen fragments and carbon-containing fragments. The lighter appended columns indicate the corresponding average charges associated with each produced fragment

used in the Coulomb explosion simulations of CH₄ (also shown Fig. 1) had an intensity of 1.1×10^{15} W/cm². This intensity was found to be optimal for inducing fragmentation of CH₄, as lower intensities (approximately 7×10^{14} W/cm² and below) led to ionization without significant fragmentation, while higher intensities (approximately 1.5×10^{15} W/cm² and above) caused complete molecular dissociation (see Table I). Intermediate laser

intensities, ranging from the ionization to the dissociation thresholds, were also explored. At intensities between the ionization and fragmentation threshold, fragmentation was less effective, often leading to partial dissociation and the formation of larger fragments, such as CH₃. At intensities between the fragmentation and dissociation threshold, smaller fragments, such as C and CH, were observed with little diversity. It is important to note

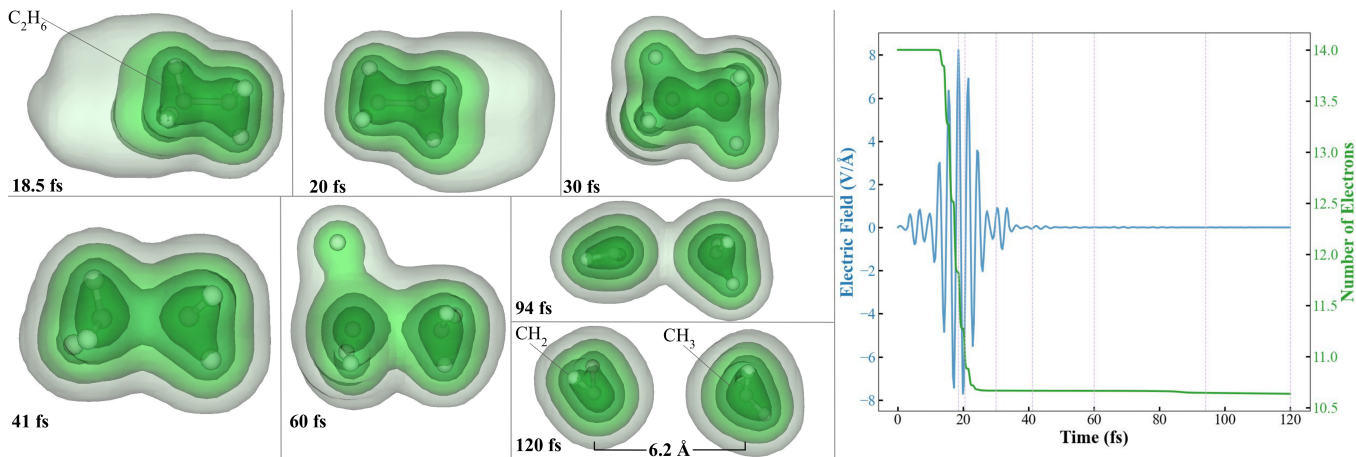


FIG. 3: Snapshots of the Coulomb explosion of C_2H_6 , illustrating the formation of CH_2 and CH_3 fragments, which carry charges of 1.18^+ and 1.18^+ , respectively (the 0.5, 0.1, 0.01, and 0.001 density isosurfaces are shown). The bar between the two fragments at 120 fs denotes the distance between their center of masses.

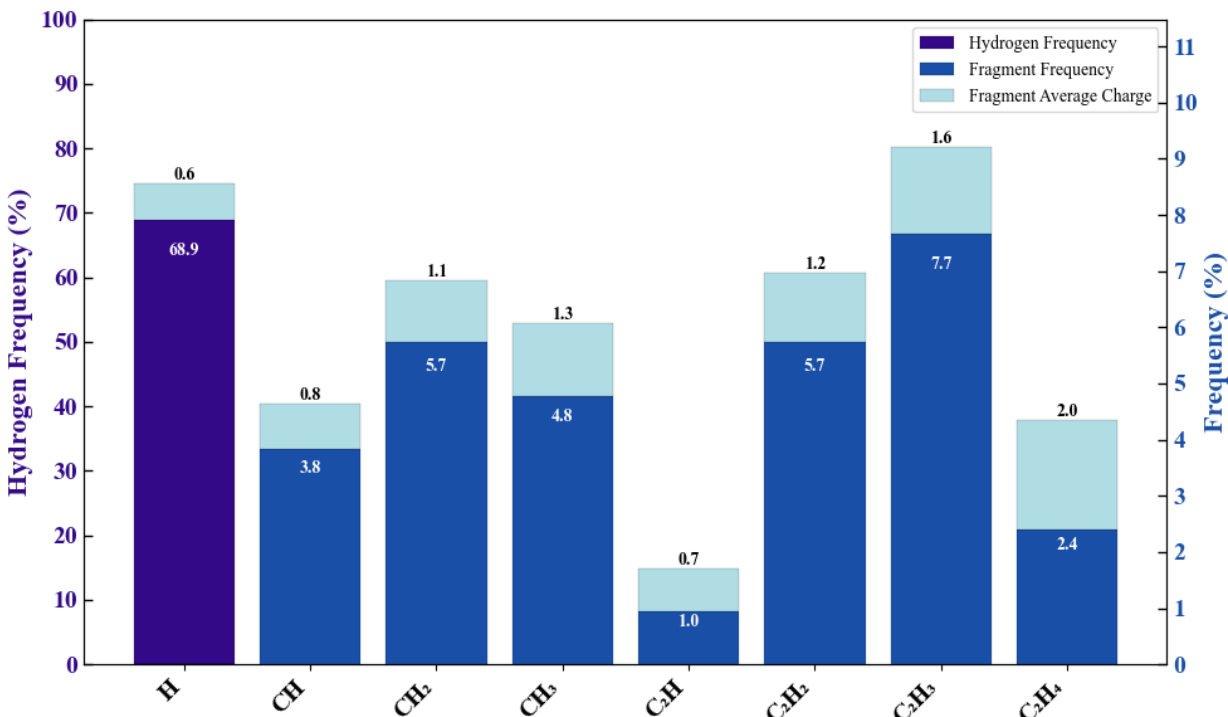


FIG. 4: Histogram illustrating the average production frequency and charge of each fragment generated in 50 C_2H_6 Coulomb explosion simulations.

that in experimental conditions, only part of the target is exposed to the highest intensity of the laser pulse, while molecules outside the focal region interact with lower intensity fields. As a result, various fragmentation processes can occur simultaneously in experiments.

Fig. 2 illustrates the distribution of fragments and their corresponding charges resulting from the Coulomb explosion of CH_4 . The plotted average production frequency represents the percentage of each fragment type relative to the total number of fragments produced. Since a sin-

gle simulation can generate multiple fragments, the total number of fragments exceeds the number of simulations. The data demonstrate that the reaction yields a range of hydrocarbons smaller than CH_4 . Among these fragments, CH is the most frequently observed carbon-containing species, appearing in 12.8% of the simulations with an average charge of 0.9^+ . Hydrogen fragments are the most commonly detected overall, with an average charge of 0.6^+ (equivalent to 0.4 electrons) as they approach the CAP. Other fragments, such as CH, CH_2 ,

and CH_3 , are also present but occur less frequently. Importantly, no CH_4 fragments were observed, indicating that the laser pulse intensity was sufficiently strong to dissociate at least one atom from the molecule in every simulation. On average, the laser ejected 2.72 electrons per simulation. These simulations help determine the optimal pulse parameters and predict the dissociation pathways for CH_4 in Coulomb explosion fragmentation.

B. Ethane (C_2H_6)

Fig. 3 presents snapshots from one of the 50 Coulomb explosion simulations with C_2H_6 as the precursor molecule. These snapshots illustrate the interaction between the electric field of the laser pulse and the electron density of the molecule. The field stretches and compresses the electron density. As shown in the pulse diagram in Fig. 3, when the electric field exceeds 5 V/\AA , between 14 fs and 22 fs, rapid ionization occurs, reducing the valence electron count to approximately 10.7. Following the dissipation of the laser pulse at 40 fs, two CH_3 fragments are produced. By 60 fs, due to the asymmetric charge distribution, one of the fragments ejects a hydrogen atom. The ionization induces strong Coulomb repulsion between the resulting fragments, causing the CH_2 and CH_3 groups to visibly repel each other throughout the simulation. Additionally, the snapshots reveal rotational motion of the fragments, particularly within the CH_2 fragment. Between 60 and 94 fs, the CH_2 molecule rotates approximately 90 degrees about the z -axis, followed by an additional 90-degree rotation from 94 to 120 fs.

The CH_2^+ and CH_3^+ fragments are well separated at the end of the TDDFT simulation in Fig. 3. Fig. 5 shows how the fragments move after 120 fs assuming that the two charged fragments interact via the Coulomb potential and their motion can be described by solving the Newton equations of motions using the Verlet algorithm. By the conclusion of the TDDFT simulation, the centers of mass of the molecules were separated by 6.2 \AA . Fig. 5 shows that the acceleration gradually decreases and the distance between the ions grows linearly. At 500 fs, the distance between the molecules increased to 45 \AA , with the CH_2^+ and CH_3^+ groups each exhibiting velocities of $6.6 \times 10^{-2} \text{ \AA/fs}$ (6600 m/s) and $4.7 \times 10^{-2} \text{ \AA/fs}$ (4700 m/s), respectively. The large difference in velocity is due to the difference between the initial velocities of the fragments. In experiment, the velocity of the CH_2^+ ion in Coulomb explosion of methanol has been measured to be 4800 m/s [47], which is within the same magnitude as in the present calculations. Considering that the laser intensity used in the simulations is six times higher than in the experiment, this agreement is remarkably good.

As depicted in Fig. 3, the laser pulse employed in the Coulomb explosion simulations of C_2H_6 had an intensity of $9 \times 10^{14} \text{ W/cm}^2$. This intensity was found to be optimal for inducing the richest diversity in fragmentation

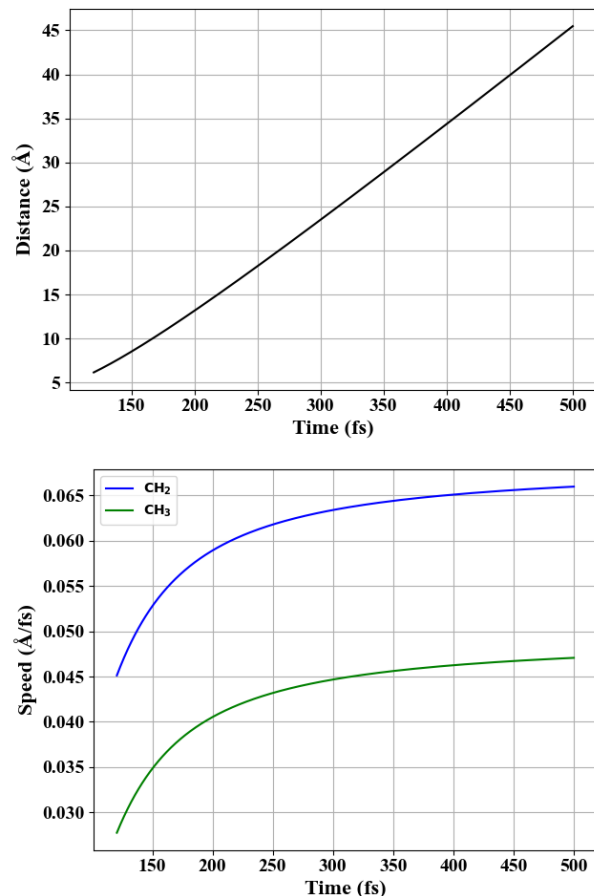


FIG. 5: Distance (top) and speed (bottom) between the CH_2 and CH_3 shown in Fig. 3 from 120 fs to 500 fs. Note that 1 \AA/fs is 100000 m/s .

pathways of C_2H_6 . To evaluate the effects of varying laser intensities, additional simulations were conducted across a broader range, extending beyond the ionization, fragmentation, and dissociation thresholds listed in Table I. It was determined that $9 \times 10^{14} \text{ W/cm}^2$ achieved the most effective fragmentation because lower intensities led to weak or incomplete dissociation (producing CH_3 or not dissociating at all) and higher intensities led to over-dissociation (producing only C_2 or complete fragmentation). Consequently, a pulse intensity of $9 \times 10^{14} \text{ W/cm}^2$ was selected for the 50 simulations, yielding the most diverse range of fragmentation pathways for C_2H_6 .

Fig. 4 shows the distribution of fragments and their corresponding charges resulting from the Coulomb explosion of C_2H_6 . The data reveal that the fragmentation produces various hydrocarbons smaller than C_2H_6 . Among these fragments, C_2H_3 is the most frequently detected carbon-containing species, appearing in 7.7% of the simulations with an average charge of 1.6^+ . Hydrogen fragments are the most prevalent overall, carrying an average charge of 0.6^+ as they are ejected from the molecule. Other fragments, including CH , CH_2 , and C_2H_3 , are also observed but with lower frequencies. No-

tably, no C_2H_6 or C_2H_5 fragments were detected, indicating that the laser pulse intensity was sufficient to dissociate at least two hydrogen atoms from the molecule in every simulation. On average, the laser ejected 3.42 electrons per simulation.

Although these results have not yet been directly compared to experimental data, they align closely with previous studies on the fragmentation of ethane [75]. That study reported various products resulting from ethane’s Coulomb explosion under different experimental conditions. Our theoretical model successfully predicts most of these fragments, except for H_2 , H_3 , and C_2H_5 . This discrepancy may arise because, at the fragmentation laser intensity threshold used in our simulations (see Table I), the model ionized an average of 3.42 electrons per molecule, compared to the single or double ionization observed in the experiments [75]. Furthermore, likely due to the higher degree of ionization, our model predicts smaller fragments such as C_2H_2 , C_2H , and CH , which have not yet been observed in ethane Coulomb explosion experiments.

C. Propane (C_3H_8)

Fig. 6 shows snapshots from one of the 50 Coulomb explosion simulations using C_3H_8 as the precursor molecule. These images depict how the laser pulse’s electric field interacts with the molecule’s electron density, stretching it and expelling it from the molecule, which leads to fragmentation. According to the pulse diagram in Fig. 6, rapid ionization occurs when the electric field intensity exceeds 4 V/\AA from approximately 14 fs to 24 fs, resulting in the retention of 14.8 valence electrons in the molecule. This ionization leads to the ejection of two hydrogen atoms at 30 fs, followed by the ejection of three additional hydrogen atoms at 55 fs. At 88 fs in the simulation, a hydrogen atom is observed transferring from the C_2H fragment to the CH fragment, indicating that molecular rearrangement and bonding can occur even after the laser-induced ionization. As illustrated in the figure, the resulting Coulomb explosion and subsequent molecular dynamics lead to the formation of C_2H and CH_2 fragments. The laser pulse employed in the Coulomb explosion simulations of C_3H_8 featured an intensity of $7 \times 10^{14} \text{ W/cm}^2$ (refer to Table I for details regarding the fragmentation pulse intensity threshold).

Fig. 7 presents the distribution of fragments and their corresponding charges resulting from the Coulomb explosion of C_3H_8 . The data reveals the diverse set of fragmentation pathways achievable with C_3H_8 as the precursor molecule, among which C_3H is the most commonly observed hydrocarbon, appearing in 2.8% of the simulations with an average charge of 1.2^+ . Hydrogen fragments are the most frequently detected overall, exhibiting an average charge of 0.6^+ as they near the CAP. Other fragments, such as CH , C_3 , and C_3H , are also present but with a lower formation rate. Importantly, no fragments

of C_3H_4 or larger were found, suggesting that the laser pulse intensity was adequate to remove at least five hydrogen atoms from the molecule in each simulation. On average, the laser expelled 5.15 electrons per simulation.

D. Butane (C_4H_{10})

Fig. 8 shows snapshots from one of the 88 Coulomb explosion simulations conducted with C_4H_{10} in the gauche conformation the precursor molecule. These snapshots capture the dynamic interaction between the laser pulse’s electric field and the electron density of the molecule, which causes the electron density to stretch and be expelled toward the CAP. As illustrated in the pulse diagram in Fig. 8, when the electric field intensity surpasses 4 V/\AA (between 14 fs and 24 fs), a rapid ionization process occurs, leaving 20.5 valence electrons in the molecule. Similarly to the previous case, by the end of the laser pulse at approximately 30 fs, two hydrogen atoms are ejected. Additionally, the CH bond involving the two hydrogen atoms at the top is significantly stretched, resulting in further ejection around 45 fs. In this instance, the system ultimately forms a charged C_2H_2 molecule along with two charged CH_2 fragments.

Fig. 8 depicts the laser pulse parameters used in the Coulomb explosion simulations of C_4H_{10} , which included an intensity of $7 \times 10^{14} \text{ W/cm}^2$. This intensity was determined to be optimal for achieving effective fragmentation of C_4H_{10} . To assess the impact of varying laser intensities on fragmentation, additional simulations were performed across a spectrum of intensities shown in Table I. It was found that, similar to the previous cases, that a particular intensity region centered around $7 \times 10^{14} \text{ W/cm}^2$ yielded the most effective fragmentation. Lower intensities resulted in insufficient dissociation, often producing larger fragments like C_2H_4 without any free hydrogen dissociation, whereas higher intensities led to excessive dissociation, resulting in only individual atoms without any bonding. Consequently, a pulse intensity of $7 \times 10^{14} \text{ W/cm}^2$ was selected for the 88 simulations to ensure a diverse range of fragmentation pathways for C_4H_{10} .

Fig. 9 displays the distribution and charges of fragments resulting from the Coulomb explosion of C_4H_{10} . The data indicate a diverse range of fragmentation products. Among these, CH_2 is the most frequently observed hydrocarbon, appearing in 6.8% of the simulations with an average charge of 0.9^+ . Hydrogen fragments are the most prevalent overall, exhibiting an average charge of 0.6^+ as they approach the CAP. Other fragments such as CH , CH_2 , and C_2H_2 are also present but occur less frequently. The laser pulse intensity was sufficient to remove at least three hydrogen atoms from the molecule in each simulation, as no fragments larger than C_3H_6 were detected. On average, the laser ejected 5.54 electrons per simulation. These results are crucial for optimizing pulse parameters and predicting the fragmentation pathways

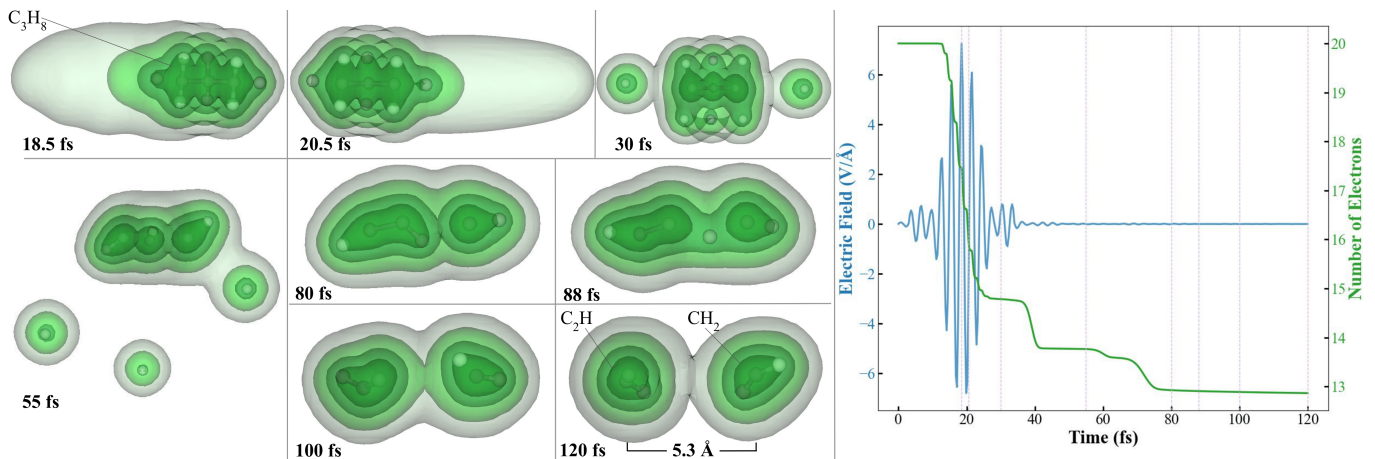


FIG. 6: C_3H_8 Coulomb explosion snapshots resulting in the formation of C_2H and CH_2 fragments with 2.22^+ and 0.91^+ charges, respectively (the 0.5, 0.1, 0.01, and 0.001 density isosurfaces are shown). The bar between the two fragments at 120 fs denotes the distance between their center of masses.

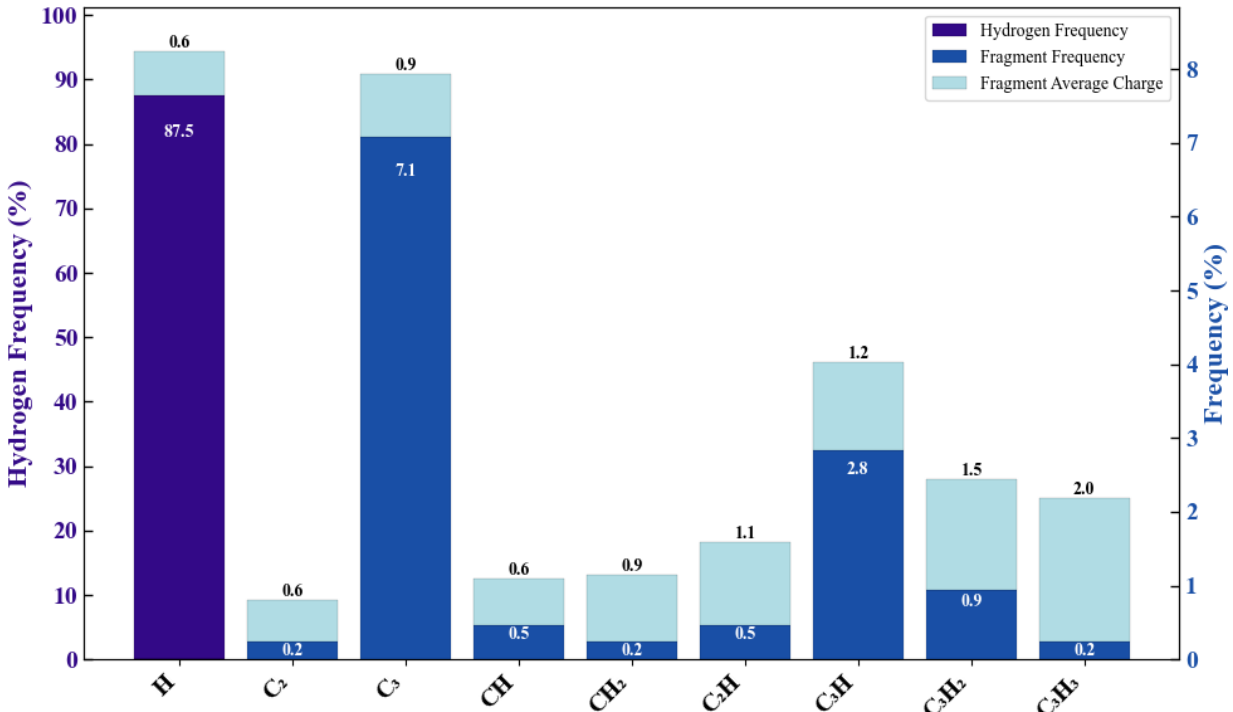


FIG. 7: Histogram illustrating the average production frequency and charge of each fragment generated in 50 C_3H_8 Coulomb explosion simulations.

of C_4H_{10} in Coulomb explosion studies.

III. SUMMARY

Fragmentation in the Coulomb explosion of hydrocarbon molecules was investigated using time dependent density functional theory simulations. This approach enables the visualization of the underlying mechanisms of fragment formation, the prediction of product formation

pathways, and the identification of ideal intensities for diverse fragmentation. We have demonstrated that at specific regions of laser intensity, hydrocarbon molecules dissociate into charged fragments consisting of n carbon and m hydrogen atoms, denoted as C_nH_m . Higher laser intensities result in the complete dissociation of the molecule, while lower intensities typically lead to the stripping of protons or cause only ionization (refer to Table I). The C_nH_m fragments can be experimentally detected [76].

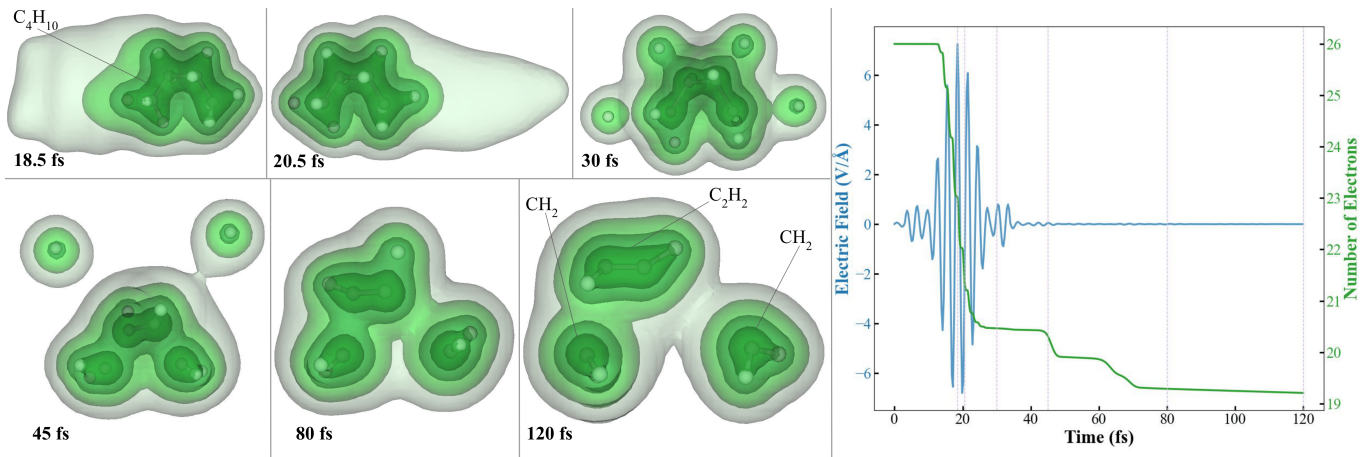


FIG. 8: C_4H_{10} Coulomb explosion snapshots resulting in the formation of C_2H_2 and two CH_2 fragments measured to have 1.12^+ , 0.77^+ and 0.90^+ charges, respectively (the 0.5, 0.1, 0.01, and 0.001 density isosurfaces are shown).

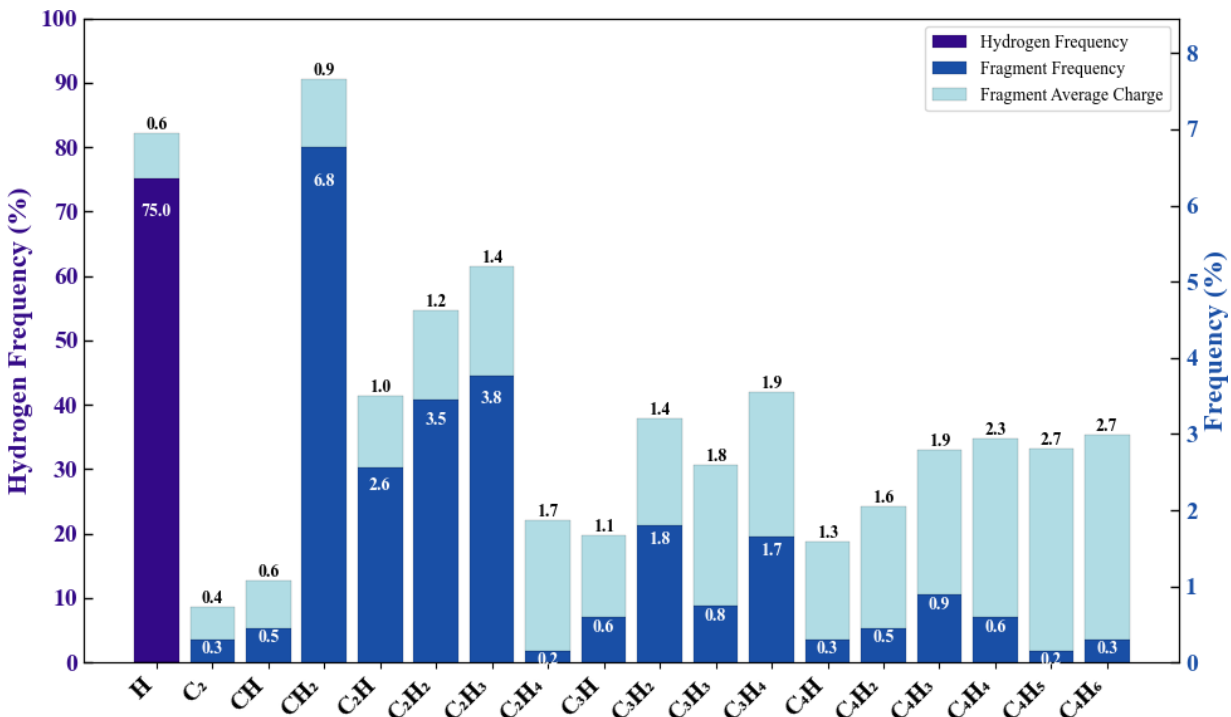


FIG. 9: Histogram illustrating the average production frequency and charge of each fragment generated in 88 C_4H_{10} Coulomb explosion simulations.

The optimal pulse intensities that yielded the most favorable fragmentation distributions for CH_4 , C_2H_6 , C_3H_8 , and C_4H_{10} were determined to be 1.1×10^{15} W/cm², 9×10^{14} W/cm², 7×10^{14} W/cm², and 7×10^{14} W/cm², respectively (as demonstrated in Table I). All other laser parameters, including wavelength, duration, and center frequency, were held constant for each molecule across their respective simulations. The electric field strength—and consequently, the intensity—was the only parameter adjusted for each molecule.

Notably, ionization of the molecule in each simulation

occurred only when the laser electric field exceeded a specific range corresponding to each molecule. Fig. 1, Fig. 3, Fig. 6, and Fig. 8 illustrate the electric field of the laser and the number of electrons in the molecule over time, demonstrating that ionization occurs approximately 5 fs before and after the peak electric field.

The initialization of velocities based on the Boltzmann distribution at 300 K facilitated the distribution of fragment products for each molecule using the same laser pulse across all simulations. The statistical distributions of fragment production frequencies provide crucial in-

sights into predicting the probabilities of various fragment formation pathways for each tested molecule. Furthermore, the average charge of the fragments indicates the likelihood of different charge states for a molecule. Fig. 9, for example, depicts an average charge of 0.6^+ for the produced CH species, which suggests that any CH fragment resulting from the Coulomb explosion has a 60% probability of being positively charged and a 40% probability of being neutral.

Moreover, a comparison of the histograms for all molecules (Fig. 2, Fig. 4, Fig. 7, Fig. 9) provides valuable insights. For instance, the average charge of the expelled free hydrogen is consistently 0.6^+ across all precursor molecules. Notable similarities are observed in the characteristics of the CH fragments as well. The two smaller alkanes (CH_4 and C_2H_6) produced CH fragments with an average charge of 0.8^+ , while the two larger alkanes (C_3H_8 and C_4H_{10}) yielded CH fragments with an average charge of 0.6^+ .

The snapshot diagrams from specific simulations illustrate the formation of fragments and bonds following the rapid ionization induced by a strong laser field. These images provide crucial insights into the discharge of electron density from the molecule and the repulsion between the resulting charged fragments. Additionally,

the snapshots enable the study of fragment dynamics after the laser-driven ionization, including structural rearrangements (Fig. 1), rotations (Fig. 3), and the transfer of atoms between different fragments (Fig. 6).

Future work could involve experimental validation of these findings to refine theoretical models, particularly by exploring different laser parameters and molecular environments. Such experimental efforts will help bridge the gap between theory and practice, providing a more comprehensive understanding of fragmentation dynamics of the Coulomb explosion.

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