Ab-initio simulation of the ionization and fragmentation of acetylene by strong femtosecond laser pulses

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Abstract. The electron and nuclear dynamics of acetylene when interacting with strong short laser pulses has been simulated in the framework of real–space Time Dependent Density Functional Theory (TDDFT) and molecular dynamics. The stretching and dissociation of individual bonds are reported, and are shown to depend on the laser field intensity and orientation relative to the laser polarization. The ionization dynamics, including ionization from individual Kohn–Sham orbitals, is also reported. The orbital ionization dynamics are shown to vary with an increase in the intensity of the laser field.

1. Introduction
The interaction of strong short laser pulses with small molecules has become an active area of recent research. Many advancements in experimental techniques have allowed the measurement of both electron and nuclear dynamics. These recent advancements include imaging of the momentum distribution of dissociated fragments with the cold target recoil ion spectrometer (COLTRIMS)[1]. The study of aligned molecules has also become possible[2, 3, 4, 5], allowing for comparison between theory and experiment without the need to average over an ensemble of molecular orientations[6]. Also among the recent experimental advancements is the ability to probe the difference in ionization from different molecular orbitals[7], and to study the ionization of individual orbitals and the sequential tunnelling of two electrons from multiple orbitals[8].

Among the ionization and fragmentation processes investigated, the Coulomb explosion has been a topic of particular interest[9, 10]. In the Coulomb explosion, the short intense laser field...
ionizes the molecule and the molecular fragments dissociate with high kinetic energy. Earlier studies of the Coulomb explosion have proposed a model of charge localization[9]. More recent studies using momentum coincidence measurements [10] point towards a theory of enhanced ionization[11, 12, 13]. Theoretically, the enhanced ionization mechanism has been investigated within Time Dependent Hartree Fock (TDHF)[14, 15, 16] for the small linear hydrocarbon, acetylene (C$_2$H$_2$). In these simulations, the ions were held fixed for the duration of the laser pulse. In this paper we use Time-Dependent Density Functional Theory[17] and Ehrenfest dynamics[18] to investigate the coupling between the electron and nuclear dynamics in acetylene under the influence of an intense short–lived laser pulse.

2. Computational Details

The electron dynamics in the simulations are 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, are represented using norm-conserving Troullier-Martins pseudopotentials [19].

The initial (ground) state of the system is first 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 equations,

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

where $k$ is a quantum number labeling the orbital. The Hamiltonian is given by,

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

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

$$\rho(r,t) = \sum_{k=1}^{N} 2|\psi_k(r,t)|^2.$$

$V_H$ is the Hartree potential, defined by

$$V_H(r,t) = \int dr' \frac{\rho(r',t)}{|r-r'|},$$

and accounts for the electrostatic Coulomb interactions between electrons. $V_{XC}$ is the exchange–correlation potential, whose exact form is a complicated functional of the entire history of the
electron density. It is approximated using the adiabatic local–density approximation (ALDA) with the parameterization of Perdew and Zunger [20]. $V_{\text{ext}}$ is the external potential, including the Coulomb potential due to the ions, $V_{\text{ions}}$, and the explicitly time–dependent potential due to the electric field of the laser $V_{\text{laser}}$. $V_{\text{ions}}$ is given by,

$$V_{\text{ion}}(r) = \sum_{i=1}^{N_{\text{ions}}} \frac{-Z_i}{|r - R_i|},$$  \hspace{1cm} (5)

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

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

$$E(t) = \hat{k} E_{\text{max}} \exp \left[ -\frac{(t - t_0)^2}{2a^2} \right] \sin(\omega t).$$  \hspace{1cm} (6)

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 $\hat{k}$ is a unit vector defining the (linear) polarization of the electric field. The Kohn–Sham orbitals are propagated with the time–evolution operator,

$$U(0, t) = \prod_q U(t_q, t_q + \delta t), \quad t_q = q \delta t,$$  \hspace{1cm} (7)

where $\delta t$ is a short time step and $t$ the total simulation time. $U(t_q, t_q + \delta t)$ is approximated with fourth-order Taylor expansion, so that the propagation of the Kohn-Sham orbitals over a short time step, $\delta t$, is given by,

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

The Kohn-Sham orbitals are represented at discrete points in real space which are organized in a uniform rectangular grid. The accuracy of the numerical calculations is controlled by adjusting the grid spacing. At the walls of the simulation cell, a zero–boundary condition is enforced. This can lead to an unphysical reflection of the wavefunction off the walls of the simulation cell. A complex absorbing potential (CAP) at the walls of the simulation cell is therefore implemented, using the form proposed by Manolopoulos[21] with an additional softening parameter which suppresses extremely large CAP magnitudes at the boundaries. As the molecule is ionized by

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{(Color online) Time–dependent fractional electron number all considered laser intensities and geometric orientations.}
\end{figure}
Figure 3. (Color online) Time–dependent occupation number of the Kohn-Sham orbitals for the parallel orientation and laser intensities of a) $14 \cdot 10^{14} \text{W cm}^{-2}$ and b) $4 \cdot 10^{14} \text{W cm}^{-2}$. 

3. Results

The interaction of acetylene, $\text{C}_2\text{H}_2$, with a linearly polarized laser pulse was investigated with TDDFT. The laser field had a full width half maximum pulse width of 4.5fs and three intensities were used: 4, 7, and $14 \cdot 10^{14} \text{W cm}^{-2}$ (see Figure 1). Parallel and perpendicular orientations of the linear $\text{C}_2\text{H}_2$ molecule relative to the laser polarization were considered.

As the acetylene molecule is exposed to a time–dependent laser field, bond stretching or even bond breaking may occur. Bond breaking where the fragments are repelled at high kinetic energy is referred to as Coulomb explosion. Figure 1 shows the distance between the hydrogen atoms and the nearest carbon atom, i.e. the C-H bond lengths. The corresponding laser fields are also shown for reference. At the lowest intensity, $4 \cdot 10^{14} \text{W cm}^{-2}$, the bond lengths are essentially unchanged. As the laser intensity is increased to $7 \cdot 10^{14} \text{W cm}^{-2}$, oscillatory bond stretching is
observed when the molecule is parallel to the laser polarization. At the high intensity, $14 \cdot 10^{14} \frac{W}{cm^2}$, some oscillatory bond stretching occurs for the perpendicular orientation and bond breaking via Coulomb explosion is observed in the parallel orientation.

In addition to the bond stretching, ionization dynamics also occur. As shown in Figure 2, as the laser intensity is increased the molecule becomes more ionized. The ionization dynamics of each molecular orbital also changes with laser intensity. As shown in Figure 3, when the molecule is in the parallel orientation and the laser intensity is $4 \cdot 10^{14} \frac{W}{cm^2}$, the highest occupied molecular orbital (HOMO) and the next highest orbital (HOMO-1), which is degenerate with the HOMO. When the laser intensity is increased to $14 \cdot 10^{14} \frac{W}{cm^2}$, the most ionized orbital is the HOMO-2, followed by the HOMO-3.

In conclusion, we have reported on nuclear dynamics and the total and orbital ionization dynamics of Acetylene when subjected to three laser fields of different intensity. The stretching and dissociation of individual C-H bonds were reported, and were shown to depend on the laser field intensity and orientation relative to the laser polarization. The orbital ionization dynamics were shown to vary with an increase in the intensity of the laser field.

4. References

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