



Investigation of intense femto-second laser ionization and dissociation of methane with time-dependent density-functional approach



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ARTICLE INFO

Article history:

Received 17 December 2013

In final form 22 April 2014

Available online 4 May 2014

ABSTRACT

Three dimensional calculations of electronic dynamics of CH₄ in a strong laser field are presented with time-dependent density-functional theory. Time evolution of dipole moment and electron localization function is presented. The dependence of dissociation rate on the laser characters is shown and optimal effective parameters are evaluated. The optimum field leads to 76% dissociation probability for GAUSSIAN envelope and 40 fs (FWHM) at 10¹⁶ W cm⁻². The dissociation probability is calculated by optimum convolution of dual short pulses. By combining of field assisted dissociation process and Ehrenfest molecular dynamics, time variation of bond length, velocity and orientation effect are investigated.

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1. Introduction

With the development of laser technology, the advent of intense laser pulses with ultra-short pulse durations, the fascinating phenomena in the main subject of laser and matter interaction and molecular dynamics have received considerable attention [1–3]. Ultra-short laser sources made the old dream of real time observation and control of chemical reactions transparent [4,5].

Irradiation of molecules with strong laser fields leads to highly nonlinear effects, including multiphoton ionization, above-threshold ionization, Coulomb explosion, dissociative recombination [6–11]. Under laser pulses with intensities more than 10¹⁵ W cm⁻² rescattering process and high harmonic generation (HHG) can be performed [12,13]. Some theoretical mechanisms have been successful in predicting the production of multiple charged molecular ions [14–16]. Due to the extra internuclear degrees of freedom in molecules and multi-orbital effects, molecular dynamics analysis is considerably complicated. This complexity is even more troublesome for polyatomic molecules, due to its difficulty of explaining the dissociation mechanism and controlling of molecular process.

There have been a number of reports focused on the interaction of intense laser field with methane molecule which can proceed in two patterns dealing with the neutral dissociation and ionic fragmentation [11,17]. Cornaggia studied the dissociation of methane, and the obtained results of multi-charged ions were interpreted on the basis of multielectron dissociative ionization over range of intensities 10¹⁵–10¹⁶ W cm⁻² [18]. Mature and co-workers studied

dissociative ionization of methane by chirped laser pulses, experimentally [19].

For strong field ionization processes, there have been many theoretical studies of diatomic molecules based on Keldysh–Faisal–Reiss (KFR) model, Ammosov–Delone–Krainove (ADK) model which can be considered as possible calculations of the strong field approximations which result in few simple theoretical expressions [20,21]. However, at the mentioned high intensities these models fail to explain some experimental observations when multielectron, inner orbital effects are considerable [22,23].

Time dependent Schrodinger equation (TDSE) provides a more complete description of the ionization processes. Kohn–Sham density-functional theory is the method for calculating the properties of large molecules [24]. This approach is based on accurate approximations, such as the local density approximation (LDA), generalized gradient approximations (GGA) and hybrids of exact exchange with GGA [25,26]. Time dependent density function theory (TDDFT) offers the theoretical description of processes in a way that it can predict reliable quantities while keeping the numerical cost low enough to be able to treat realistic systems [27,28]. The time dependent electron localization function (TDEL) can provide a good insight into complex reactions, time resolved observation of the formation and breaking of the chemical bonds [29]. Another possible ab initio molecular dynamics (AIMD) scheme that fits into the TDDFT framework is Ehrenfest molecular dynamics, which uses the electron–nuclei separation and the Wentzel–Kramers–Brillouin (WKB) classical limit [30]. In the earlier works the dissociation of only diatomic molecules and rarely tri-atomic molecules are investigated. However, at the present work, we concentrate on the multi-atomic molecule of methane, one of the major greenhouse gases with high global warming

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potential. Developing and applying advanced technologies in the area of dissociation and conversion of methane into valuable higher hydrocarbons is the interest of recent experimental researches and some measurement is reported.

Following our recent studies on the dissociation of methane with semi-classical approach and one dimensional calculation of electronic dynamics [31–33], a three dimensional theoretical study of dissociation yields of CH₄ is presented. Calculations are carried out for CH₄ molecule, a symmetry molecule and using accurate TDDFT. In this Letter a clear method by combining of two proper methods of field assisted dissociation and Ehrenfest molecular dynamics is introduced to investigate the dissociation of a multi-atomic molecule and orientation dependence of strong laser field dissociation, properly.

The aim is to study the effect of laser parameters including different shapes of laser pulses and various arrangements with delay time between dual short pulse, different intensities and various pulse durations on the dissociation probability. For a better presentation of the molecular dynamics and proper analysis of time-dependent process, three approaches are justified. The first is numerical model of the TDSE with TDDFT, the second is TDEL and the third is simple Ehrenfest molecular dynamics model. According to semi-classical approach, molecule dissociates spontaneously due to the stretching of their chemical bonds. With optimum convolution of a dual short pulse, the dissociation probability of 70% is obtained. This is due to the possibility of femtosecond pulse shaping to control the desired product pathways. The calculated results are explained in detail in the following.

2. Theoretical and computational methods

2.1. Time-dependent density-functional approach of strong field dissociation

The molecular dynamic and electronic structure of CH₄ is studied by solving Schrödinger/Kohn–Sham equations with TDDFT. In this work, a numerical grid in the three dimensional real space with sphere box shape, using an appropriate absorber at the edge of the grid is utilized. The exchange–correlation (xc) potential with GGA approximation is characterized to investigate the electronic structure of methane with high accuracy.

The electron density $\rho(\mathbf{r}, t)$ is determined by

$$\rho(\mathbf{r}, t) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \psi_{i\sigma}^*(\mathbf{r}, t) \psi_{i\sigma}(\mathbf{r}, t), \quad (1-1)$$

σ , i and N_{σ} are spin index, orbital index and the number of electrons with σ spin, respectively. $\Psi_{i\sigma}(\mathbf{r}, t)$ satisfies the TD Kohn–Sham equation, in atomic unit. The Kohn–Sham potential is separated in the following way

$$\begin{aligned} i \frac{\partial}{\partial t} \psi_{i\sigma}(\mathbf{r}, t) &= \left\{ -\frac{\nabla^2}{2} + V_{Ksh}(\mathbf{r}, t) \right\} \psi_{i\sigma}(\mathbf{r}, t) \\ &= \left\{ -\frac{1}{2} \nabla^2 + V_{ne}(\mathbf{r}) + V_H(\mathbf{r}, t) + V_{xc}(\mathbf{r}, t) + V_{ext}(\mathbf{r}, t) \right\} \\ &\quad \psi_{i\sigma}(\mathbf{r}, t), \end{aligned} \quad (1-2)$$

$V_{ne}(\mathbf{r})$ is the nucleus–electron potential of the coulomb interaction between electron and nuclei, $V_H(\mathbf{r}, t)$ is Hartree potential of electron–electron coulomb interaction, $V_{xc}(\mathbf{r}, t)$ is the exchange–correlation potential and $V_{ext}(\mathbf{r}, t)$ is the external potential.

Generalized gradient approximation in exchange–correlation potential is utilized as [34]:

$$V_{xc}(\mathbf{r}, t) = \frac{\partial}{\partial \rho(\mathbf{r}, t)} \left[\int \varepsilon_{xc}(\rho(\mathbf{r}, t), \nabla \rho(\mathbf{r}, t)) \rho(\mathbf{r}, t) d\mathbf{r} dt \right], \quad (1-3)$$

ε_{xc} is the exchange–correlation energy density with functional dependence on the density $\rho(\mathbf{r}, t)$ and $\nabla \rho(\mathbf{r}, t)$.

$V_{ext}(\mathbf{r}, t)$ describes the interaction with the laser field. Using the dipole approximation it is expressed as

$$V_{ext}(\mathbf{r}, t) = f(t) \mathbf{E}_0 \sin(\omega t) \cdot \mathbf{r}, \quad (1-4)$$

where \mathbf{E}_0 , $f(t)$ and ω denote the peak field strength in the Z direction, the temporal profile and the carrier frequency, respectively.

Time evolution of the wave function is obtained as

$$\psi_{i\sigma}(\mathbf{r}, t + \Delta t) = \exp(-i(\hat{T} + \hat{V}_{Ksh}(\mathbf{r}, t))\Delta t) \psi_{i\sigma}(\mathbf{r}, t), \quad (1-5)$$

\hat{T} and $\hat{V}_{Ksh}(\mathbf{r}, t)$ are kinetic energy and Kohn–Sham potential, respectively.

Split-operator technique exploits time dependent segment of above equation and it is defined as

$$\begin{aligned} \exp(-i(\hat{T} + \hat{V}_{Ksh}(\mathbf{r}, t))\Delta t) &= \exp(-i\hat{V}_{Ksh}(\mathbf{r}, t)\Delta t/2) \exp(-i\hat{T}\Delta t) \\ &\quad \exp(-i\hat{V}_{Ksh}(\mathbf{r}, t)\Delta t/2) + O(\Delta t^3), \end{aligned} \quad (1-6)$$

The propagation wave function is implemented by

$$\begin{aligned} \psi_{i\sigma}(\mathbf{r}, t + \Delta t) &= \exp(-i\hat{V}_{Ksh}(\mathbf{r}, t)\Delta t/2) F^{-1} \{ \exp(-i\hat{T}\Delta t) \\ &\quad F[\exp(-i\hat{V}_{Ksh}(\mathbf{r}, t)\Delta t/2) \psi_{i\sigma}(\mathbf{r}, t)] \}, \end{aligned} \quad (1-7)$$

where F and F^{-1} represent the fast Fourier transform from coordinate space to momentum space and inverse fast Fourier transform from momentum to coordinate space, respectively. Dissociation of a molecule under the effect of a strong laser field occurs through the initial ionization of the molecule, followed by the fragmentation of molecular ions. Methane is a symmetric molecule without a permanent dipole moment and the dynamic alignment may not have a main contribution to the angular dependence of the dissociation fragments. Molecular excitation with these intense lasers can be interpreted as a transition from the bound state to the repulsive state and breaking four C–H bond lengths.

The total dissociation probability is calculated from a sum over the populations of all non-bound states or, alternatively, one minus the sum over all bound state populations which can be obtained by

$$P_{diss} = 1 - \sum_i^{\text{bound}} |\psi_{i\sigma}(\mathbf{r}, t) \rangle \langle \psi_{i\sigma}(\mathbf{r}, t)| \quad (1-8)$$

Dissociation probability is calculated for interacting CH₄ molecule under Ti: Sapphire laser pulse with wavelength of 800 nm, pulse durations of 10–40 fs over range of intensities 10¹⁴–10¹⁶ W cm⁻² and various pulse shapes using octopus code [35]. A numerical grid are defined as $\Delta \mathbf{r} = 0.1 \text{ a.u.}$ and $\Delta t = 0.0005 \text{ fs}$ with using an appropriate soft absorber at the edge of the grid. The radius of the spherical simulation box is 40a.u. and absorber is applied between 20a.u. and 40a.u. which smoothly brings down the wave function without spurious reflections. Fragmental ions (e.g., CH₃⁺, CH⁺, C⁺, C²⁺) created from photo-ionization process over a range of laser intensities 10¹⁴ W cm⁻² to 10¹⁵ W cm⁻² are formed by Coulomb explosion. The fragments of C³⁺, C⁴⁺ are dominant via Coulomb explosion and tunneling ionization. At the intensities larger than 10¹⁶ W cm⁻², removal of a carbon K-shell electron from methane proceeds via tunneling and rescattering ionization, without the influence of molecular channels [36].

If the C–H bond length of methane molecule becomes more than 6 Å during the laser irradiation time, molecule will be dissociated [37]. Therefore, we assume the electron density that leaves this volume during the interaction with the laser field represents non-bound states.

Time evolution of the dipole moment after an interaction with laser pulse is calculated as an expectation value of the electron radius vector with the time-dependent electron density,

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