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Dissociative ionization of methane in an elliptical pulse shaped laser field

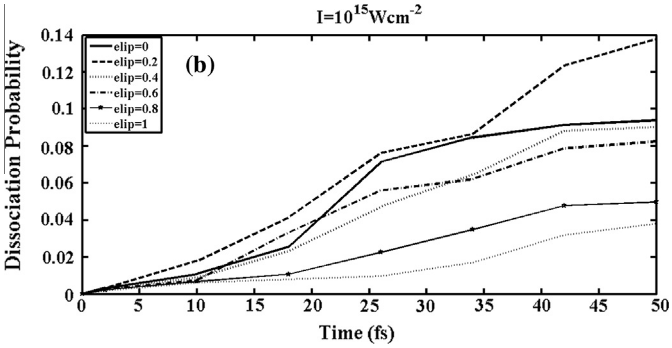
E. Irani, R. Sadighi-Bonabi *, A. Anvari

Department of Physics, Sharif University of Technology, P.O. Box 11365-9567, Tehran, Iran

HIGHLIGHTS

- Three dimensional calculation of dissociative ionization of CH_4 is presented with TDDFT.
- The ellipticity dependence of the dissociation probability at intensities from 10^{14} W cm^{-2} to 10^{16} W cm^{-2} is presented.
- Optimum convolution of dual short pulses and two-color mixed nonresonant laser pulses are analyzed in the dissociation probability.
- An ellipticity dependence of dissociation probability with amount of almost 70% for $\varepsilon = 0.2$ at 10^{15} W cm^{-2} intensity is determined.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of strong femto-second laser pulses on the dissociation probability of methane has been investigated analytically in various arrangements. The ellipticity dependence of the dissociation probability at intensities from 10^{14} W cm^{-2} to 10^{16} W cm^{-2} for Ti:Sapphire laser is presented. A reliable calculation of the dissociation probability based on 3D time-dependent Schrodinger equation with an improved model of time-dependent density-functional theory is presented. These calculations are carried out for three different cases of elliptically polarized laser pulse, optimum convolution of dual short pulses, and two-color mixed nonresonant laser pulses. It is found that the rescattering contribution of the laser pulses to the fragmental yields is more remarkable for $\varepsilon = 0.2$, at 10^{15} W cm^{-2} laser intensity. Furthermore, by using the dual pulses combination for three proposed conditions, extracted by semi-classical approach, the dissociation rates up to 78% is achieved. In addition, by using a two-color mixed laser pulse, the total dissociation probability is improved up to 50% in comparison to a single pulse.

Introduction

The rapid advance in the development of high power ultra-short pulse lasers have been stimulated the realistic expectation of using such devices in producing energetic particle beams for application in various fields [1–3]. These particles could also be used in generation of X-rays and transmutation of hazardous materials [4,5]. Many researchers have developed several experimental and theoretical methods using intense laser pulses to have deeper insight into the molecular dynamics, ionization, dissociation and coherent control of photochemical reactions [6–10]. They have identified several mechanisms to explain the ionization and dissociation of molecules in intense laser fields. These processes include multi-photon ionization (MPI), above threshold ionization (ATI), coulomb explosion (CE), explosive photo-dissociation (EPD), rescattering

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* Corresponding author. Tel.: +98 2166164526; fax: +98 2166022711.
E-mail address: sadighi@sharif.ir (R. Sadighi-Bonabi).

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process and high harmonic generation (HHG) [11–13]. The dissociation of a molecule under the effect of intense laser field occurs through the initial ionization of the molecule, followed by the fragmentation of molecular ions. The other method also considers how a molecule in the super-excited state (SES) is dissociated and induces neutral fragments [14]. The rescattering process can be illustrated by a three-step model including tunneling ionization, acceleration of electrons and recollision [15]. When an elliptical laser field is used the returning electrons can be adjusted to control multi-electron nonsequential ionization (NSI) and HHG [16]. The processes behind molecular ionization in the strong laser filed were revealed by using linearly and circularly polarized pulses [17]. Elliptically polarized laser field by an elasticity of $\varepsilon = 0.1$, lead to a peak in double ionization in benzene molecule [18]. At the ultra-intense elliptically polarized laser fields, the molecular alignment and angular dependence of the ionization probability present a major effect on the symmetry of the molecular orbitals which can have the main role on the ionization processes [19].

In recent years, considerable efforts have been made in the realization of coherent control of chemical reactions by using laser pulse shapers which is based on the manipulation of wave packets to a desired reaction channel [20–22]. Fundamental theories for pulse shaping involve solving a time-dependent variation method to optimize the performance index related to a reaction of interest and the predefined desired target. Time dependent Schrodinger equation (TDSE) provides a more complete description of the ionization processes. Kohn-Sham density-functional theory is a method for calculating the properties of large molecules. In this method due to replacement of the interacting many electron problem with an effective single particle problem, it can be solved more quickly [23]. This approach is based on accurate approximations, such as the local density approximation (LDA), the generalized gradient approximations (GGA) and the hybrids of exact exchange with GGA [24,25]. Time dependent density function theory (TDDFT) can predict reliable quantities while keeping the numerical cost low enough to be able to treat realistic systems [26,27]. This method is a useful tool for extracting the dynamics of excited electrons. Due to the extra internuclear degrees of freedom and multi-orbital effects, molecular dynamics analysis and controlling of the molecular dynamics of polyatomic molecule in the ultra-strong laser field is considerably complicated. Due to these inherent limitations few simple theoretical expressions of the strong field dynamics for large molecules are presented and a complete theoretical study that can explain dissociation process and controlling dynamics is desired.

The capability of controlling the motion of molecules by a laser pulse in order to guide a chemical reaction into a desired thermally inaccessible state is an active research area in strong field science. Based on the Judson and Rabitz report, by combining the pulse shaping techniques with genetic and learning algorithms, one can find tailored pulses for proper controlling the chemical reactions [28]. Although, great improvements are achieved in controlling chemical reactions by these methods, initial experimental data and expensive controlling cost is needed. To the best of our knowledge, only few theoretical expressions with limited explanations for optimal control theory are implemented beyond two atomic molecules. Methane is a primary fossil fuel and the conversion of methane into heavier hydrocarbons and hydrogen has many advantages [29]. These products may provide new feed stocks for chemical processes. One of the attractive methods is using intense pulse lasers without any catalysts. The control of organic chemistry with intense femto-second laser fields capable of controlling a system toward prescribed desired valuable products has been a main goal. By developing and applying advanced technologies, conversion of methane into valuable higher hydrocarbons is the interest of recent experimental researches and some measurement is reported [30,31].

In the present work, following our recent studies on the dissociation of multi-atomic molecules [32–34], three dimensional (3D) theoretical study of enhanced strong field dissociation yield for CH_4 molecule by using femtosecond pulses at intensities in the range of 10^{14} W cm^{-2}–10^{16} W cm^{-2} is presented. The strong dependence of the dissociation rate on the laser characters including different arrangements with delay time between dual short pulses, ellipticity dependence and two-color mixed nonresonant laser pulses is shown and the optimal effective parameters to produce the maximum dissociation yield are evaluated. The obtained results are explained in detail in the following.

Theoretical and computational method

The molecular dynamic and dissociation process of CH_4 is investigated by solving Schrödinger/Kohn-Sham equations and time-dependent density-functional approach. In this work, a numerical grid in three dimensional real space with sphere box shape is used. The TD-LB$_\alpha$ exchange–correlation (xc) potential is characterized to investigate the electronic structure of methane molecule and non-trivial many body effects.

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

$$\rho(\mathbf{r},t) = \sum_{\sigma}\sum_{i=1}^{N\sigma}\psi^{*}_{i\sigma}(\mathbf{r},t)\psi_{i\sigma}(\mathbf{r},t), \tag{1}$$

σ, i and N_σ are spin index, orbital index and the number of electrons with σ spin, respectively.

Time-dependent Kohn-Sham equations for N-electron systems in the TDDFT framework is given by

$$i\frac{\partial}{\partial t}\psi_{i\sigma}(\mathbf{r},t) = \left\{-\frac{1}{2}\nabla^2 + V_{ne}(\mathbf{r}) + V_H(\mathbf{r},t) + V_{\mathrm{xc}}(\mathbf{r},t) + V_{ext}(\mathbf{r},t)\right\}\psi_{i\sigma}(\mathbf{r},t), \tag{2}$$

$V_{ne}(\mathbf{r})$ is the potential of electron interaction with the nuclei, $V_H(\mathbf{r},t)$ is Hartree potential of electron-electron coulomb interaction, $V_{\mathrm{xc}}(\mathbf{r},t)$ 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 [35]:

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

$\varepsilon_{\mathrm{xc}}$ is the exchange–correlation energy density with functional dependence on the density $\rho(\mathbf{r},t)$ and $\nabla\rho(\mathbf{r},t)$. The potential $V_{ext}(\mathbf{r},t) = -E(t)\cdot\mathbf{r}$, represents the interaction with the external laser field.

The elliptically polarized laser pulse is described by

$$E(t) = E_0 f(t)\left(\frac{1}{1+\varepsilon^2}\right)^{1/2}[\sin(\omega t)\mathbf{z} + \varepsilon\sin(\omega t - \pi/2)\mathbf{x}], \tag{4}$$

where E_0, $f(t)$, ε and ω denote the peak field strength, temporal profile of the laser pulse, ellipticity ($0 \leqslant \varepsilon \leqslant 1$) and the carrier frequency, respectively.

The propagated two-color mixed nonresonant pulses which have the nonresonant pulse frequency ω and the overtone 2ω is assumed as

$$E(t) = E_0 f(t)\sin(\omega t) + E_0 f(t)\sin(2\omega t), \tag{5}$$