Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Selective photo-dissociative ionization of methane molecule with TDDFT study

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ARTICLE INFO

ABSTRACT

Three dimensional calculation of control dynamics for finding the optimized laser filed is formulated using an iterative method and time-dependent density functional approach. An appropriate laser pulse is designed to control the desired products in the dissociation of methane molecule. The tailored laser pulse profile, eigenstate distributions and evolution of the efficient occupation numbers are predicted and exact energy levels of this five-atomic molecule is obtained. Dissociation rates of up to 78%, 80%, 90%, and 82% for CH_2^+, CH^+, C^+ and C^{++} are achieved. Based on the present approach one can reduce the controlling costs.

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1. Introduction

One of the attractive methods in the dissociation of molecules is using intense pulse shaped lasers. Interaction of strong laser fields with molecules leads to nonlinear effects, including multiphoton ionization, above-threshold ionization, tunneling and rescattering ionization, Coulomb explosion, charge resonance enhanced ionization, and field assisted dissociation and high harmonic generation [1–5]. Recent progress of control of electron wave packets, probing of nuclear and electronic dynamics, imaging of molecular orbitals with ultra-fast laser pulses have key roles for coherent control of photochemical reactions [6–8]. The capability of controlling the dynamic of molecules by ultra-short laser pulse in order to transfer an initial state to a desired thermally inaccessible state was suggested by Tannor et al. in 1985 [9]. The visualization and analysis of the dynamics of chemical bonds shortly implemented by real time observations of the transition-state region between reactants and products in 1994 [10]. The pulse shaping technology had developed over the last decades, and the experimental optimal control had translated from theoretical methods to a unique experiment by Judson and Rabitz [11]. For more complex systems and clusters, a feedback loop, together with a learning algorithm are used to achieve the preferred goal [12].

Quantum optimal control theory (QOCT) provides the necessary tools to the tailored theoretical design of the laser pulses for controlling a molecular system towards preferred reaction pathways [13]. For strong field ionization and dissociation processes, there have been many theoretical studies which can be considered as possible calculations of the strong field approximations which result in few simple theoretical expressions [14–15]. However, at the mentioned high powerful lasers, these models fail to explain some experimental observations when multielectron roles, inner orbital effects and ion-electron interactions are considerable [16]. Due to these inherent limitations exact numerical solutions of the strong field dynamics for the large molecules did not exist and a complete theoretical study for controlling dynamics is still attractive and desirable. Recently, only global mathematical procedure is suggested to use OCT with time-dependent density functional theory (TDDFT) for a quantum system by Castro et al. [17]. To the best of our knowledge, no theoretical calculations for selective quantum optimal control of desired fragments are reported beyond the two atomic molecules due to their complexity of orbitals, inner electron effects and the numerous interaction forces among them.

The present work, concentrates on the dissociation of methane molecule, one of the major greenhouse gases, and the control of reactions into the valuable fragments. The valuable fragmental ions of CH_2^+, CH^+, C^+ and C^{++} created from 10^{14}–10^{15} W cm^{-2} intensity range are formed by Coulomb explosion. Due to the multi-orbital effects, molecular dynamics analysis and controlling of molecular dynamics is considerably complicated. In this paper, following our ecent theoretical and experimental studies on the dissociation of methane [18–20], the optimized laser field via convolution strategy of TDDFT with QOCT is obtained. The focus is to improve the dissociation rate and selective control of the dissociation path by considering the modified pulse shapes to facilitate several possible transitions in a multi-atomic molecule. This approach extracts the exact dynamics of the excited electrons and time evolution of the most important occupation numbers by suitably tailored laser pulse and also an exact energy diagram can be presented. Based on the obtained energy diagram,

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dissociation pathways are clearly identified for valuable ionic fragmentations of CH_2^+, CH^+, C^+ and C^{++}. Indeed, the great improvements of dissociation rates are achieved in controlling product ratios of desired products with theoretically designed laser field. The simulations indicate that direct closed loop control in the laboratory operates effectively with less complexity and low cost method.

This paper is organized as follows. In Section 2, time-dependent density functional approach and quantum optimal control scheme are introduced to provide tailored femtosecond laser pulses for an enhanced dissociation rates and capable of controlling a system towards the prescribed products. In Section 3, the calculated results are explained in detail. The paper is concluded in Section 4.

2. Computational method

2.1. Time-dependent density functional approach

In this calculation, a numerical grid in the three dimensional real space are used as $\Delta r = 0.01$ a.u. and $\Delta t = 0.02$ a.u. This is controlled by the variable radius of sphere box shape [21–24]. The radius of spherical simulation box is 30 a.u. and the box is surrounded by absorbing boundaries of a $\sin^2$-type imaginary absorber at the edges of grid which smoothly brings down the wave function without spurious reflections. In order to study spatial asymptotic effects on the exchange-correlation (XC) potential, the time-dependent Kohn-Sham equations are numerically solved with different XC potentials. The XC potential with TD-LB$_\alpha$ potential is more accurate to investigate the electronic structure of methane and dissociation yields [25].

The electron density $\rho(\mathbf{r}, t)$ at the electron coordinate $\mathbf{r}$ and time t is determined by

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

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 time dependent Kohn-sham equation, in atomic units. The Kohn-Sham potential is conventionally separated in the following way

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

$V_{ne}(\mathbf{r})$ is the potential of electron interaction with the nuclei, $V_H(\mathbf{r}, t)$ is Hartree potential, $V_{xc}(\mathbf{r}, t)$ is TD-LB$_\alpha$ (van Leeuwen-Baerends) exchange-correlation potential. $V_{ext}(\mathbf{r}, t)$ is the external potential which describes the interaction of molecule with the laser field and it is expressed rely on dipole approximation as follows

$$V_{ext}(\mathbf{r}, t) = f(t)\mathbf{E}_0 \sin(\omega t).\mathbf{r}, \tag{3}$$

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

The propagation of wave function is implemented by second order split-operator scheme

$$\psi_{i\sigma}(\mathbf{r}, t_0 + \Delta t) = \exp(-iV_{Ksh}(\mathbf{r}, t)\Delta t/2)F^{-1}\{\exp(-iT\Delta t) \tag{4}$$
$$F[\exp(-iV_{Ksh}(\mathbf{r}, t)\Delta t/2)\psi_{i\sigma}(\mathbf{r}, t_0)]\} + O(\Delta t^3),$$

T and $V_{Ksh}(\mathbf{r}, t)$ are kinetic energy and Kohn-Sham potential, respectively. Within the temporal duration of the laser pulse, the potential

surfaces are modified by the laser field and if the laser intensity is strong enough, it can induce the ion dissociation fragments. Methane is a symmetric molecule and the ground electronic state configuration of the five doubly occupied molecular orbitals is $(1a_1)^2(2a_1)^2(1t_2)^6$. Molecular excitation with these intense lasers can be interpreted as a transition from the bound state to the unbound state and breaking C—H bond lengths as one minus the projection to 40 lowest eigenstates. The electron density that leaves 18 a.u.–50 a.u. box radius, during the interaction with the laser field with wavelength of 800 nm and intensity in the range of 10^{14}–10^{15} W cm^{-2} represents unbound states and molecule will be dissociated. This box radius approximately agrees with the spatial extent of 40 lowest eigenstates. The total dissociation probability is calculated from a sum over the populations of all unbound states or, alternatively, one minus the sum over all bound state populations which can be calculated by

$$P_{diss} = 1 - \sum_i^{bound} |\langle\psi_i(\mathbf{r})|\psi(\mathbf{r}, t)\rangle|^2 \tag{5}$$

Dissociation probability is calculated for interaction of CH_4 molecule with initial intense Ti: Sapphire laser pulse with pulse duration of 20 fs (FWHM), rectangular envelope and peak laser intensities in the range of 10^{14} W cm^{-2}–10^{15} W cm^{-2} using octopus code [26].

2.2. Pulse optimization with quantum optimal control theory

QOCT is used for finding the optimized laser pulse that guides the molecular system to predefined products with the maximum efficiency. The results are promising by combining of QOCT with TDDFT in order to obtain an accurate energy diagram and identify dissociation pathways for valuable ionic fragmentations. The shape of laser pulse is now capable to cover the other transitions for several possible pathways, properly. In this efficient and low cost method, without requiring experimental data, an optimum pulse shape with the maximum yield is introduced. The objective of optimal control theory can be formulated as an optimal laser pulse $\varepsilon(t)$ which drives the state $|\Psi(\mathbf{r}, t)\rangle$ of the system in a finite time interval T from an initial state $|\Phi_i\rangle$ to a prescribed target state $|\Phi_f\rangle$. The optimum condition corresponds to the maximum of following overlap functional

$$J_1 = |\langle\psi(\mathbf{r}, T)|\phi_f\rangle|^2, \tag{6}$$

To adjust the significance of the laser intensity, the total fluence of laser pulse is weighted with a penalty factor α

$$J_2 = -\alpha\left[\int_0^T dt\varepsilon^2(t) - E_0\right], \tag{7}$$

where E_0 is the initial fluence. Finally, the system obeys the time-dependent Schrödinger equation, that the state $|\Psi(\mathbf{r}, t)\rangle$ actually represents a time-evolved quantum state. This can be expressed by

$$J_3 = -2Im\int_0^T dt\langle\kappa(\mathbf{r}, t)|(i\partial_t - H(\mathbf{r}, t))|\psi(\mathbf{r}, t)\rangle, \tag{8}$$

$\kappa(\mathbf{r}, t)$ is a Lagrange multiplier. The optimal laser pulse $\varepsilon(t)$ for the transition of initial state into favorite final state maximizes the total functional $J = J_1 + J_2 + J_3$.