

Computer modeling of photoinduced dissociation of ethylene molecule by short IR laser pulse

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1. INTRODUCTION

How to excite a molecule to a selected vibronic state? How to control over an excitation of a molecule? These questions are of great importance for molecular spectroscopy and laser chemistry.¹ A way to control over molecular excitation by IR laser pulse is to use frequency-swept (chirped) pulses. The idea of such an excitation discussed over the past few decades¹⁻³ is illustrated in Fig. 1.

In order to excite a harmonic oscillator, one should fit the excitation frequency to that of the oscillator. By contrast, for anharmonic oscillator the efficiency of such an excitation will be much lower due to the anharmonicity. To overcome this difficulty, the pulse frequency should follow the vibrational level spacing $\omega_\lambda = \omega_{k+1} - \omega_k$ (see Fig. 1). As a result the efficiency of the excitation will be enhanced. In addition, frequency sweeping is a powerful tool for control over the vibrational mode's energy exchange, because of its phase sensitivity.

There is a limited number of experimental works on this problem. Enhanced population transfer from the lowest level to the highest level in the three-state ladder $5s \rightarrow 5p \rightarrow 5d$ of rubidium atom by chirped ultrashort laser pulses was experimentally observed in Ref. 4 (see also the references therein). The excitation of C_2H_4 molecule by chirped ultrashort IR laser pulses was investigated in Ref. 5.

The theoretical investigation of the dynamics of an excited molecule based on running the wave packets' dynamics or on solving the Schrödinger equation is bounded in practise by the case of diatomic molecules.^{2,3} Here we present a theoretical model which is suitable for running the Molecular Dynamics of multiatomic molecules excited by a laser pulse. Using this model, we revealed the features of the chirped pulsed laser excitation of C_2H_4 molecule.

There are some qualitative considerations³ which prove the validity of using the method of classical Molecular Dynamics (MD) for describing the dynamics of a multiatomic molecule under the conditions where quasistochastic quasiclassical contribution to the Liouville operator is much greater than the quantum contribution due to anharmonicity. In any case, to prove the validity of classical MD, it is necessary to run a computer modeling and to compare its results with the experimental data.

We present here the results of MD simulation of the dynamics of ethylene molecule (C_2H_4) excited by picosecond IR laser pulse. The parameters of the potential energy surface described by the Molecular Mechanics (MM) method⁶, were determined using fitting method described in Ref. 7. With the parameters, the molecule's dynamics, the temporal dependence of its total energy, and its power emission spectrum were calculated.

2. COMPUTER SIMULATION RESULTS

We describe the molecule's dynamics using the classical Hamiltonian equations for nuclei coordinates and momenta, with the potential function⁷ which is supplemented with the Hamiltonian of interaction of the molecule with the laser field

$$\mathcal{H}_I = - \sum e_k \vec{r}_k \vec{E}_L(t).$$

Charge distribution is introduced here by the set of effective charges e_k which correspond to separate atoms. The initial conditions for \vec{r}_k, \vec{p}_k are represented by pseudorandom numbers, which simulate fluctuations produced by the quantum thermal equilibrium distribution at temperature T . To simulate this distribution, we introduce the set of Gaussian random values for the fluctuations of coordinates and momenta of normal modes λ , so that their energies are equal to energies predicted by Plank formula

$$\epsilon_\lambda = \hbar\omega_\lambda / [\exp(\hbar\omega_\lambda/kT) - 1].$$

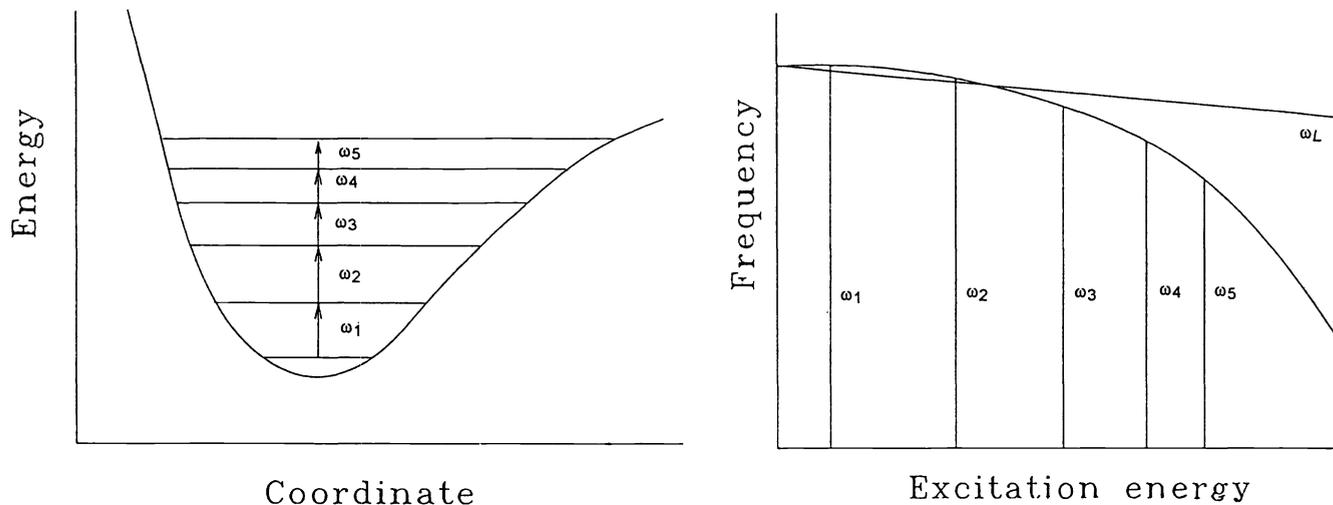


Fig. 1. The potential energy function of an anharmonic oscillator (a) and the frequency-sweep dependence (b) such that the frequency ω_L follows the vibrational level spacing; ω_k are the vibrational frequencies.

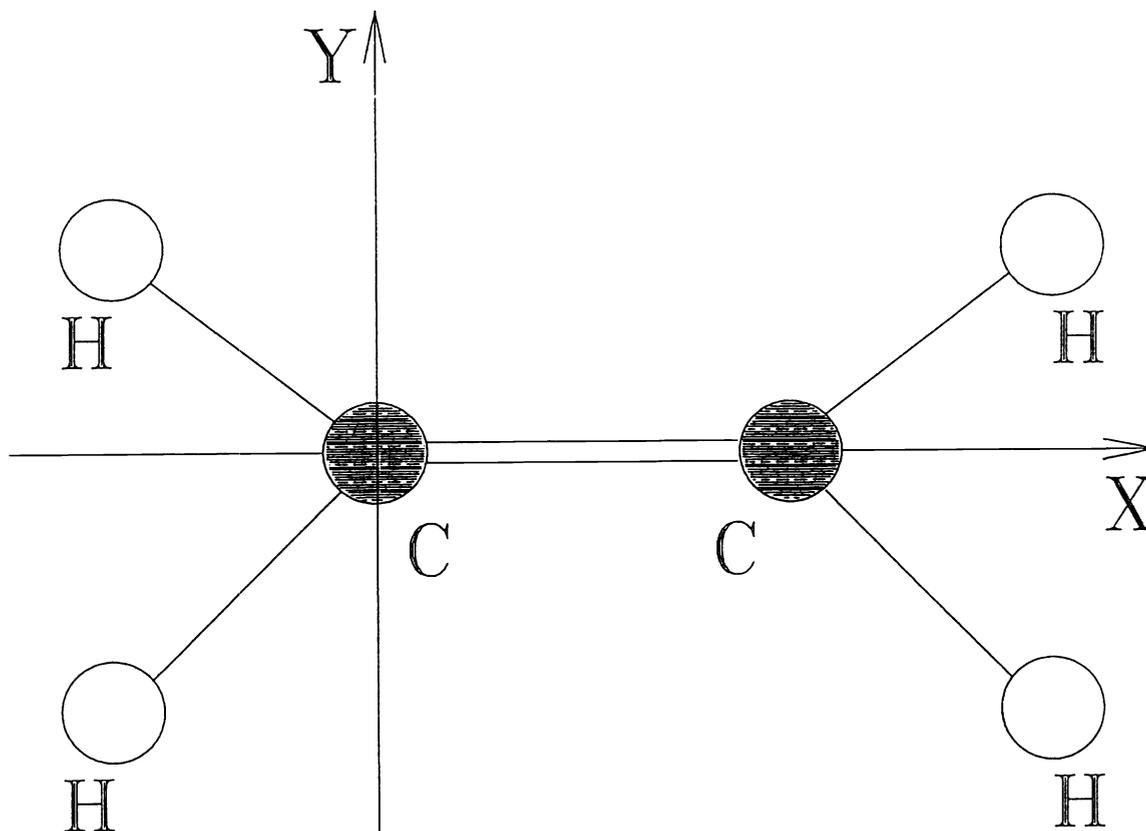


Fig. 2. The equilibrium configuration of an ethylene molecule.

These fluctuations are the fluctuations of the center of the wave packet which describes the molecule in terms of quantum theory, when the packet is disturbed by the equilibrium temperature fluctuations. These fluctuations produce the corresponding incoherent thermal radiation of the molecule. This radiation is included in the calculated spectral characteristics of individual molecule, in addition to the coherent response to the external field. In order to separate the coherent component of the molecule's radiation, one should simulate not a single molecule but the proper ensemble of molecules. The rotational fluctuations must be taken into account by introducing fluctuations of the total angular momentum resulting in the corresponding fluctuations of momenta $\delta\vec{p}_k$. In the majority of our calculations the temperature is taken to be zero, to make more clear the dependencies due to the processes of intramolecular energy exchange.

The equilibrium configuration of ethylene molecule is represented in Fig. 2. Laser field is described by a Gaussian pulse with the duration $\tau_p = 1-10$ ps and the frequency assumed to be linear function of time t :

$$\vec{E}_L(t) = E_0 \vec{e} \cos \varphi(t) \exp[-4(t - t_c)^2 / \tau_p^2],$$

$$\varphi(t) = \omega_{L0} t + (1/2)(d\omega_L/dt)t^2.$$

Here ω_{L0} is the initial laser frequency, t_c is the moment of time when the field intensity is equal to its maximum value. The field intensities are chosen in the interval $I = 10^9 - 10^{13}$ W/cm². The polarization \vec{e} is orthogonal to the plane of molecule, i. e., it is parallel to the vector of dipole moment of the out-of-plane vibration (along z-axis).

The first step of computer modeling is the determination of MM parameters of a molecule using the available data.⁷ The next step is calculating of time dependencies of coordinates $\vec{r}_k(t)$ and the total energy $E(t)$. With the help of two-dimensional computer visualization of $\vec{r}_k(t)$, $E(t)$ and of three-dimensional dynamics of the molecule, it is possible to investigate the qualitative dependencies between the characteristics of molecular excitation and parameters of the pulse.

There are two regions of laser intensities that has been investigated in this work:

- The region of moderate fields with $I \leq 10^{11}$ W/cm², where a molecule does not dissociate and its motion is relatively regular;
- The region of strong fields with $I \geq 10^{12}$ W/cm², where molecules undergo quasistochastic motion and can dissociate into two or several fragments.

In Fig. 3 the dependence of total energy $E(t)$ normalized to its maximum is represented for the chirp-free pulse with $\tau_p = 6$ ps and the temperature $T = 0$ K. Similar dependencies for the pulse with positive linear chirp and for the pulse with the negative chirp, with the same frequency deviation of about 1 %, are represented for the intensities $I = 10^9$, 10^{10} , and 10^{11} W/cm². The maximum value of the field amplitude is achieved at $t_c = 6$ ps.

In the case of chirp-free pulse one can see the oscillations of the total energy of a molecule, despite the exact resonance of laser frequency with the out-of-plane mode oscillations of C₂H₄ molecule.

The more intense is the field, the faster are the molecular oscillations. At the end of the pulse the molecule preserves a significant part of its maximum energy only at minimum intensity $I = 10^9$ W/cm². Such a behavior is explained by changing of the eigenfrequency of the excited mode due to its anharmonicity. For a harmonic oscillator the total energy should grow steadily and be a quadratic function of time for a square pulse.

Chirping enlarges the amount of a total energy preserved in a molecule after the pulse is over, as soon as the conserved energy dependence on field intensity remains the same. The ratio of the total energy preserved in a molecule to its maximum value for the chirp-free pulse yields the value $E_+/E_0 = 3.2$ at $I = 10^9$ W/cm². For the case of a pulse with a negative chirp this value yields $E_-/E_0 = 6.5$. Therefore, a negative chirp is more consistent with the form of potential surface of ethylene molecule. Nevertheless, both types of chirping are effective. Hence, the effective force constant for the out-of-plane mode varies non-steadily as a function of the excitation rate.

The spectral distributions of the third harmonic in the spectrum of fluorescence for $I = 10^9-10^{11}$ W/cm² are shown in Fig. 4 for the chirp-free excitation. The general qualitative rule is enriching of spectra with the increase in intensity. This fact can be accounted for by increasing of intermode exchange with the increase of excitation rate of a molecule.

For moderate fields the major part of the molecule's energy is stored in the resonant mode, and the processes of intermode exchange are relatively small. In the case of strong fields the molecule dissociates. During the excitation the nuclear motion becomes chaotic resulting, in particular, in spontaneous breaking down of initial symmetry of the molecule (the vibrations of different H-atoms and C-atoms are not identical, though at $T = 0$ and $\vec{e} \parallel z$ they should be identical because of the symmetry of the potential function). Nevertheless, the pulse parameters still

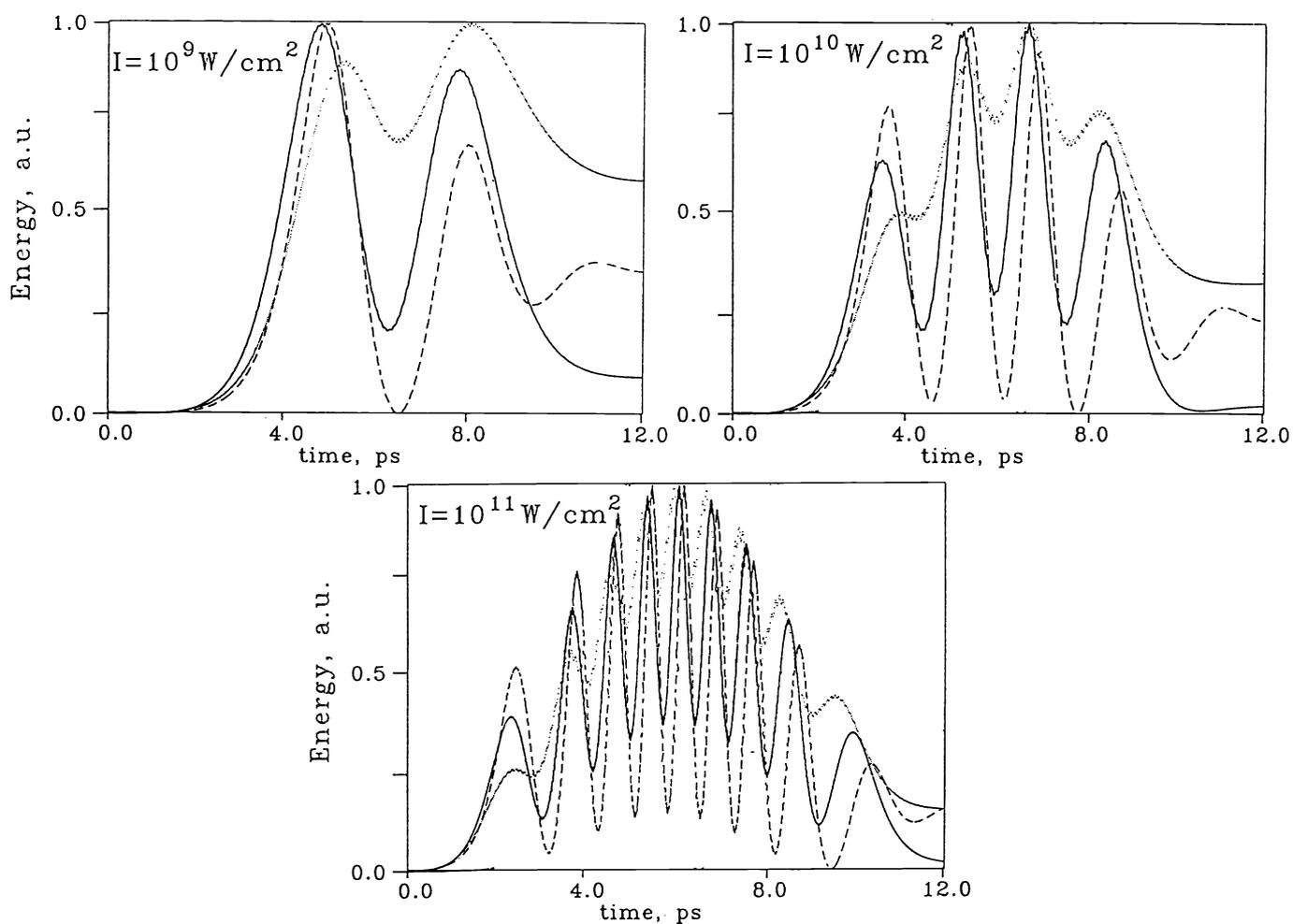


Fig. 3. Total energy of C_2H_4 molecule under excitation at $I = 10^9$, 10^{10} , and 10^{11} W/cm^2 . Pulse duration is equal to 6 ps; chirp is equal to 0 % (solid line), +1 % (dashed line) or -1 % (points) of vibrational frequency.

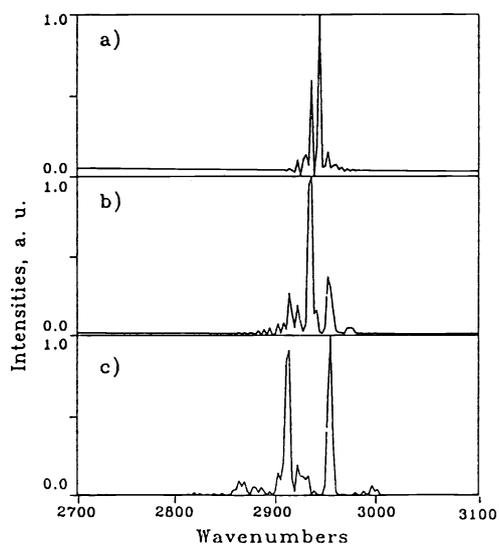


Fig. 4. Fluorescence spectrum of the third harmonic at $I = 10^9$ (a), 10^{10} (b), and 10^{11} W/cm^2 (c).

affect the reaction dynamics due to both the initial non-chaotic stage of the excitation process and the details of interaction of the chaotic molecular vibrations with the external field. At lower intensities the main reaction channel is the breaking of one hydrogen bond. In this case, using of chirp allows one to reduce the dissociation threshold (Fig. 5). At higher intensities all the other channels are possible. As an example, the reaction $C_2H_4 \rightarrow CH_2 + CH_2$ is shown in Fig. 6. Hence, one can control the reaction channel by varying the chirp parameters. There is only one difficulty, that is, there is no simple recipe for choosing the optimal parameters.

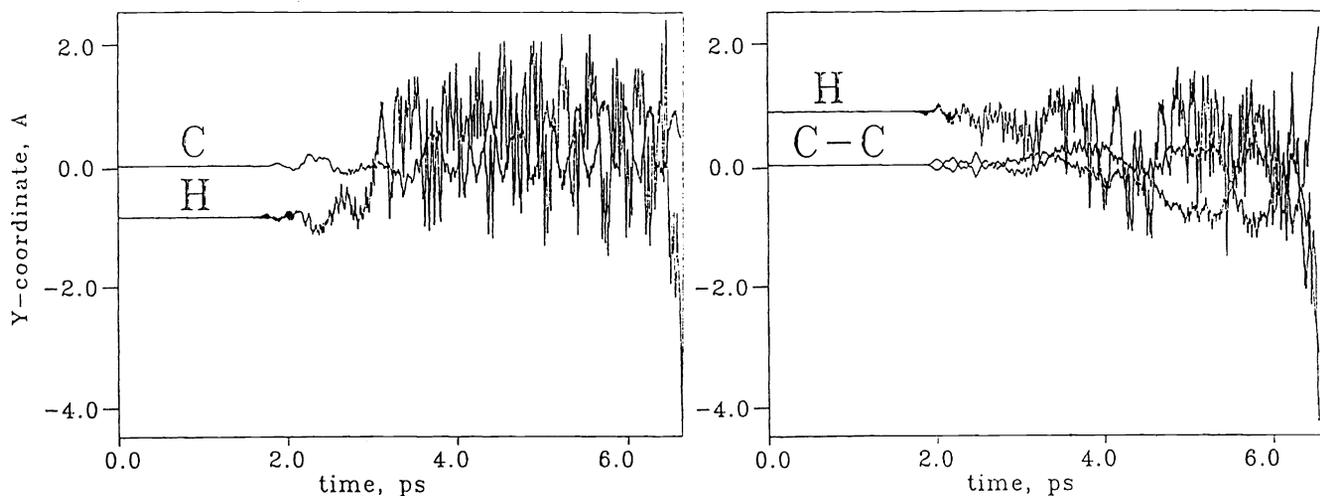


Fig. 5. $C_2H_4 \rightarrow C_2H_3 + H$ dissociation reaction of C_2H_4 molecule excited by IR laser pulse with linear positive chirp of about 15 % to laser frequency. Pulse duration is equal to 4.4 ps, energy density is equal to 40 J/cm^2 .

Fig. 6. $C_2H_4 \rightarrow CH_2 + CH_2$ dissociation reaction of C_2H_4 molecule excited by IR laser pulse. Pulse duration is equal to 4.4 ps, energy density is equal to 44 J/cm^2 . Laser frequency is in resonance with the mode 949 cm^{-1} .

3. REFERENCES

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