

Multiphoton ionization of inner-valence electrons and fragmentation of ethylene in an intense Ti:sapphire laser pulse

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Abstract

Using linearly polarized 200 fs Ti:sapphire laser pulses the multiphoton ionization and fragmentation of ethylene was studied. A model is proposed which is able to satisfactorily predict the abundance of the different fragments, $C_2H_4^+$, $C_2H_3^+$ and $C_2H_2^+$ as a function of laser intensity. It is shown that fragmentation of the molecule occurs as a result of multiphoton ionization of inner-valence electrons followed by radiationless transitions to various dissociation channels of the molecular ion. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The interaction of hydrocarbons with intense ultrafast laser pulses is promising in terms of the potential application of intense field multiphoton processes to mass spectroscopy due to pulse lengths and radiative transitions being now shorter than intramolecular relaxation rates. Such application requires a detailed study of the ionization at high intensities and a satisfactory model for predicting the rate of dissociation and fragmentation of these molecules. Our finding on modeling of the rate of intense field multiphoton ionization (MPI) of hydrocarbons [1] coupled to the recently established picture of fragmentation of ethylene molecule interact-

ing with single-photon short-wavelength laser pulses [2–5], provides a model for predicting the abundance of the fragments of this molecule in interaction with longer-wavelength pulses where many photons are involved in the process. In the electronic ground state, the neutral planar ethylene molecule has the electronic configuration $1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2$ [6]. While the MPI of any one of the two electrons from the outermost orbital ($1b_{3u}$) will result in a $C_2H_4^+$ ion in its ground electronic state (X^2B_{3u}), the MPI of an inner-valence electron will produce an excited molecular ion which is usually unstable and undergoes fragmentation. For example, if any of the electrons of the ($1b_{3g}$) orbital is ionized via MPI, the molecular ion would be in its first excited electronic state (A^2B_{3g}). However, radiationless transitions will bring back the population of the excited electronic state down to the highly excited ro-vibrational levels of the ground electronic state of the ion in a short time of order of 10^{-14} s [7]. The ion created in this manner can redistribute its internal energy by disso-

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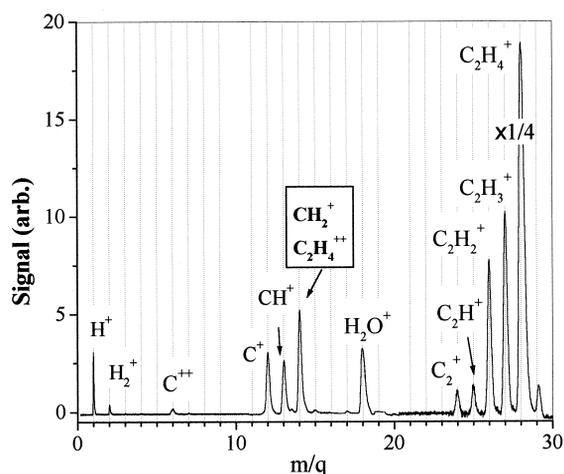
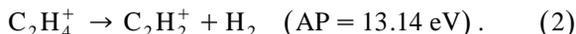


Fig. 1. Mass spectrum of C_2H_4 interacting with linearly polarized Ti:sapphire laser pulses at a peak laser intensity of 2×10^{14} W/cm². The signal of $C_2H_4^+$ was divided by 4.

ciating through one of the following channels



Here AP denotes the appearance potential, it is the minimum energy needed to form a particular fragment from a neutral molecule in its ground state. Note that these APs are for the field free case, while in the presence of an intense laser pulse they might be reduced appreciably due to field-induced barrier suppression [8–10] such that the molecular ion produced in any of the levels of the A^2B_{3g} state will undergo the fragmentation process through coupling with the deformed ground electronic state. The sequence of the events which could lead to the fragmentation of the molecule to $C_2H_3^+$ or $C_2H_2^+$ fragments can be summarized as follows: (1) MPI of an electron from the inner-valence orbital $1b_{3g}$ which results in an ion in the excited electronic state, A^2B_{3g} ; (2) radiationless transition of the population from this state to the high-lying ro-vibrational levels the ground electronic state; and (3) the fragmentation of the molecular ion. Thus, to find the rate at which any of the two ionic fragments $C_2H_3^+$ or $C_2H_2^+$ are produced, it is sufficient to calculate the rate of the MPI of the electrons from the $1b_{3g}$ orbital. In the present Letter, adopting this simple idea, we show

that the rate of fragmentation of C_2H_4 molecules interacting with a Ti:sapphire laser pulse can be predicted very well.

2. Results and discussion

The mass spectrum of the C_2H_4 molecules interacting with a Ti:sapphire laser operating at 800 nm, with a transform limited pulse length of 200 fs is presented in Fig. 1. The experimental setup and procedure are discussed elsewhere [11]. The intensity of the laser is around 2×10^{14} W/cm². Even at this high intensity the signal of $C_2H_4^+$ ions is higher than that of any of the fragments (note that we have divided the signal of $C_2H_4^+$ by 4.0).

In Fig. 2 the ion yield vs. peak laser intensity curves (ion curves) of $C_2H_4^+$ and its fragments are shown. The ion curves of $C_2H_3^+$ and $C_2H_2^+$ fragments, having similar dependence on laser intensity,

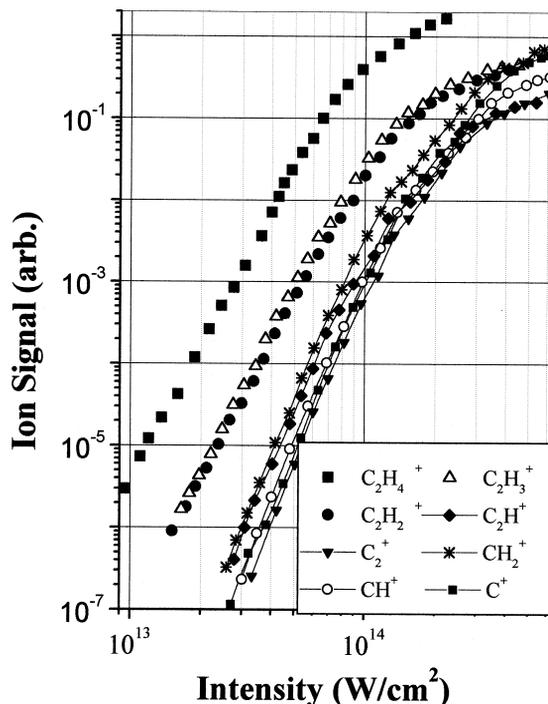


Fig. 2. The ion curves of different fragments of C_2H_4 created as a result of interaction of ethylene with a linearly polarized Ti:sapphire laser pulse.

nearly follow the ion curve of $C_2H_4^+$ and saturate at the same intensity as the ion curve of $C_2H_4^+$. This indicates that the process leading to the two fragments has nearly the same nonlinear order (meaning the number of photons involved in the process) as the process of the MPI to $C_2H_4^+$. The ion curves of other fragments (C_2H^+ , C_2^+ , etc.) increase with intensity faster than the ion curve of $C_2H_4^+$. Therefore the process leading to these fragments is of higher order and probably has a close link to the MPI to $C_2H_4^{++}$. In the present Letter we will not discuss the mechanism of fragmentation to these smaller fragments and instead we will focus on the $C_2H_3^+$ and $C_2H_2^+$ fragments.

In Fig. 3 we present the ion curves of $C_2H_4^+$, $C_2H_3^+$ and $C_2H_2^+$. We have also included theoretical

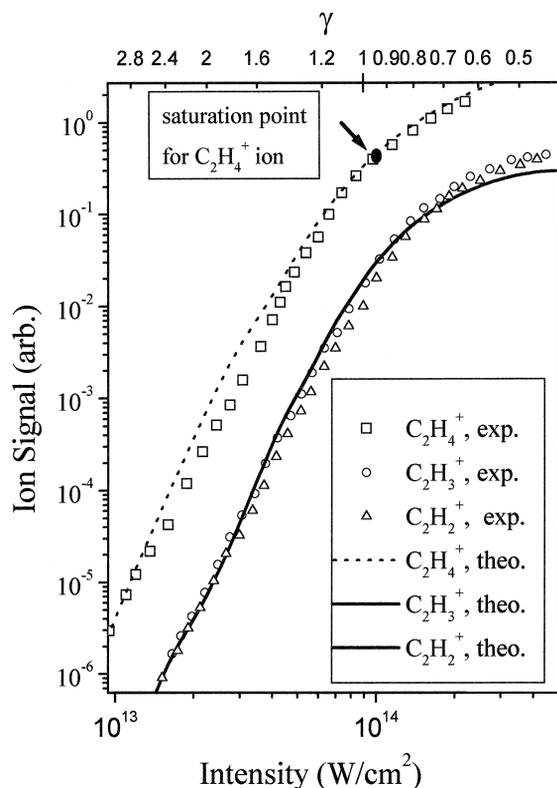


Fig. 3. The ion curves of $C_2H_4^+$, $C_2H_3^+$ and $C_2H_2^+$. The upper horizontal scale is the γ scale (Keldysh parameter) for ethylene. The theoretical curves are the result of calculation based on the fragmentation model as explained in the text. Note that the theoretical curve of $C_2H_2^+$ overlaps with that of $C_2H_3^+$.

ion curves of the three ions which were calculated in the following manner. As we stated above, to calculate the rate of dissociation of ethylene to the two fragments, it is sufficient to calculate the rate of MPI from the inner valence orbital, $1b_{3g}$. We denote the rate of MPI from the $1b_{3u}$ and $1b_{3g}$ orbitals by W_1 and W_2 , respectively. Then the rate equations for the probability of ionization to the ground and the first excited electronic states of ion, P_1 and P_2 is written as

$$\begin{aligned} \frac{dP_0}{dt} &= -\left(\sum W_i\right)P_0 \\ \frac{dP_i}{dt} &= -W_iP_0 \end{aligned} \quad (i = 1, 2). \quad (3)$$

Here, P_0 is the probability of the molecule to remain neutral.

To solve these equations, the rate of MPI, W_i , as a function of the laser intensity is needed. For this purpose we use the results of Ref. [1], from which the cycle averaged rate of the MPI of a two carbon hydrocarbon like ethylene with ionization potential E_i in a linearly polarized laser field with peak electric field strength F and frequency ω is given by

$$\begin{aligned} W &= \sum_{n=N}^{\infty} 2\pi\omega^2 p(n - n_{\text{osc}})^2 \\ &\times \int d\Omega |FT(I(\mathbf{r})\Psi(\mathbf{r}))|^2 J_n^2\left(n_f, -\frac{n_{\text{osc}}}{2}\right), \end{aligned} \quad (4)$$

where $N \equiv [n_{\text{osc}} + E_i/\omega]$ is the minimum number of photons necessary to ionize the molecule, $n_{\text{osc}} = F^2/\omega_3$ is the oscillation energy of an electron in the field, $J_n(u, v)$ is the double Bessel function [12], $p = \sqrt{2\omega(n - n_{\text{osc}} - E_i/\omega)}$ and $n_f = 2\sqrt{n_{\text{osc}}/\omega} \cos(\theta)$, where θ is the angle between the momentum of the electron, \mathbf{p} , and the electric field of the laser, \mathbf{F} . In Eq. (4), FT stands for the Fourier transform operator. The function $\Psi(\mathbf{r})$ is the asymptotic wavefunction and $I(\mathbf{r})$ accounts for the Coulomb correction for the single-electron tunneling

model [13,14]. Following Ref. [13] these functions are given by;

$$\Psi(\mathbf{r}) = C_{n^*l^*} (\sqrt{2E_i})^{3/2} (r\sqrt{2E_i})^{n^*-1} \times \exp(-r\sqrt{2E_i}) Y_{lm}(r/r), \quad (5)$$

$$I(\mathbf{r}) \equiv \left(\frac{2Z_c^2}{n^*Fr} \right)^{n^*}. \quad (6)$$

where

$$|C_{n^*l^*}|^2 = \frac{2^{2n^*}}{n^*\Gamma(n^*+l^*+1)\Gamma(n^*l^*)}, \quad (7)$$

with $l^* = n^* - 1$ and $n^* = \sqrt{2E_i}/Z_c^2$. Here, Z_c (in units of electronic charge) is given by $Z_c = 1.0 + Q$, where Q is the net charge that has migrated from the H atoms onto the C sites. From the ab initio wavefunction of ethylene, Q is calculated to be approximately -0.2 [15]. For the MPI of the inner-valence electrons, the value of Z_c is found simply by using the fact that the ionization potential is proportional to Z_c .

Before proceeding further we should address the domain of validity of Eq. (4). Apart from neglecting intermediate discrete levels, the main limitation to the applicability of this equation is the accuracy of the Coulomb correction which is reflected in the function $I(\mathbf{r})$ of Eq. (6). An analysis presented in Ref. [16] shows that this correction should be valid if

$$\gamma \ll \gamma_{cr}, \quad (8)$$

where

$$\gamma \equiv \sqrt{2\omega^2 E_i} / F \quad (9)$$

is the Keldysh parameter [17] and γ_{cr} is defined as the limiting value of γ for which the following equation has a real solution for the dummy variable, τ .

$$\frac{1}{\gamma} \left(\cosh(\tau) - 1 - \frac{\tau}{2} [\sinh(\tau) - \gamma] \right) = \left(\frac{\tau\gamma}{\gamma_k [\sinh(\tau) - \gamma]} \right)^{1/2}, \quad (10)$$

where

$$\gamma_k = 2E_i / (n^*\omega). \quad (11)$$

For the MPI of ethylene the value of γ_{cr} is calculated to be ~ 3.05 . Our experimental result on the MPI of rare gas atoms [13] has shown that the criterion expressed by Eq. (8) is too strong and in practice the criterion $\gamma < \gamma_{cr}$ is good enough for real experiments. It is impossible to give a more precise empirical relationship because γ_{cr} is species dependent. This should be contrasted to the case of pure tunneling where the ADK formula [18] is valid. In this case, a precise empirical relationship for its validity, namely, $\gamma < 0.5$ is provided [19]. We note that the current Krainov's model [14] bridges the gap between pure tunneling and pure multiphoton regimes, and answers a long standing question of finding a satisfactory model for this 'no man's land'. From the upper scale of Fig. 3, it is seen that our experiment is being done in the range of $\gamma < \gamma_{cr}$ so that using Eq. (4) is justified.

To apply Eq. (4) in our case we make the following considerations. Firstly, the effect of the Franck–Condon factors on the rate of MPI must be included in the calculation. In an exact treatment

$$W_i = \int f(E) W(E_i + E) dE, \quad (12)$$

where $W(E_i + E)$ is given by Eq. (4), only E_i is replaced by $E_i + E$ (E_i is the adiabatic ionization potential of the molecule) and $f(E)$ is the Franck–Condon factor for the transition from the ground state of the neutral molecule to those ro-vibrational levels of the electronic state i of the ion with an energy E above the minimum of the adiabatic potential surface i . In our calculations we used the Franck–Condon factors deduced from the photo-electron spectra of ethylene [6,20] and neglected any effect that the presence of the laser field might have on the Franck–Condon factors. However, our numerical calculation shows that neglecting the Franck–Condon factors (i.e., taking $W_i = W(E_v)$ instead of Eq. (12), where E_v is the vertical ionization potential of the molecule) does not change the curves of Fig. 4 appreciably. Secondly, since W in Eq. (4) strongly depends on the laser intensity (note that $F = 5.33 \times 10^{-9} \sqrt{I}$, where F is the field in atomic units and I is the intensity in W/cm^2) through n_{osc} and n_f , an

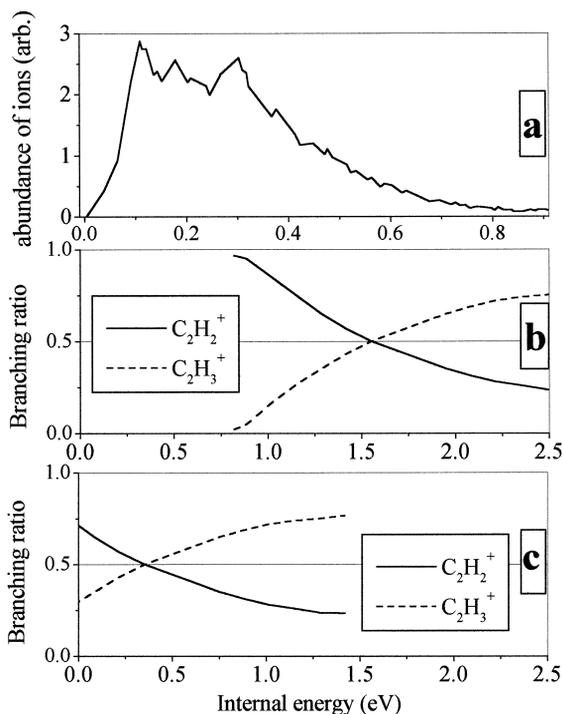


Fig. 4. (a) The relative abundance of molecules which ionize to A^2B_{3g} state with internal energy E calculated for a laser intensity of 6×10^{13} W/cm². (b) The branching ratios of $C_2H_2^+$ and $C_2H_3^+$ ions from Ref. [21]. (c) The branching ratio curves shifted to lower internal energies as a result of decrease in the appearance potential of the ions.

analytical formula for the spatial and temporal dependence of the intensity is desired. For our experiment $I(\mathbf{r}, t)$ is given by [22].

$$I(\mathbf{r}, t) = \frac{I_0}{\sqrt{1 + \left(\frac{\lambda z}{\pi w_0^2}\right)^2}} \exp\left(-2 \frac{(r/w_0)^2}{1 + \left(\frac{\lambda z}{\pi w_0^2}\right)^2}\right) \times \exp\left[-(4 \ln 2) \left(\frac{t}{\tau}\right)^2\right], \quad (13)$$

where $\lambda = 800$ nm is the wavelength, I_0 is the peak intensity, $w_0 = 49$ μ m is the $1/e^2$ radius of the focal spot and $\tau = 200$ fs is the full width at half maxi-

mum (FWHM) of the pulse. Finally, the three-dimensional Fourier transform in Eq. (4) is calculated using Hankel transforms [23].

Equipped with all these, Eqs. (3) were solved and the time- and position-dependent probabilities $P_1(\mathbf{r}, t)$ and $P_2(\mathbf{r}, t)$ were determined. The number of each type of ion, N_i , is then calculated from

$$N_i = \int_V \int_{-\infty}^{\infty} P_i(\mathbf{r}, t) dt dV, \quad (14)$$

where V is the interaction volume. To compare the calculated ion curves with the experimentally measured ones we use the saturation behavior of the ion curves as a reference point (the saturation intensity is at the point – illustrated by the arrow in Fig. 3 – where the ion curve changes slope). Due to the type of the detector we used (electron multiplier tube), it is very difficult to know the precise number of ions detected in each shot. To compare a theoretically calculated ion curve with the experimental one it is sufficient to multiply the measured signal by a factor to bring the theoretical and the measured ion curves at the same level in their respective saturation intensities. Noting that the abundance of the $C_2H_3^+$ and $C_2H_2^+$ ions is nearly the same in our experiment, we assume that the molecular ions ionized to A^2B_{3g} state dissociate with equal probabilities through the two channels 1 and 2. As a result, the theoretical curves of the two ions ($C_2H_3^+$ and $C_2H_2^+$) overlap. Our assumption can be justified as the following. In Fig. 4a we present the relative abundance of molecules which ionize to A^2B_{3g} state with internal energy E (the factor $f(E)W(E_i + E)$ in Eq. (12)). In Fig. 4b the branching ratios of $C_2H_2^+$ and $C_2H_3^+$ are presented as functions of the internal energy of the ion [21]. As we mentioned in Section 1, in the presence of laser fields the APs are lowered. This is equivalent to shifting the curves of Fig. 4b towards lower internal energies. In analogy with the case of H_2^+ ion [8,9] the lowering in the APs, ΔE , is estimated as $\Delta E \approx 0.5 FR$, where R is the size of the ion and F is the strength of the field. For example, at a laser intensity of 6×10^{13} W/cm² and assuming a size of $R \sim 2$ au, ΔE will be around 1.1 eV and the branching ratio curves will be shifted to lower internal energies as it is shown in Fig. 4c. In this case the branching ratios of both fragments will

average to 0.5 over the range of internal energies for which the relative abundance of ions is appreciable ($0 < E < 0.7$ eV in Fig. 4a).

As it is observed from Fig. 3, the fit between the experiment and the theory is excellent. This is an indication of the legitimacy of the proposed model and the approximations which we made in our calculations. The approximations were the following: (1) mainly the π electrons are ionized; (2) the Frank–Condon factors are independent of laser intensity; (3) due to the presence of an intense laser pulse the molecular ion produced in any of the levels of the excited electronic state, A^2B_{3g} , undergoes the fragmentation process through coupling with the deformed ground electronic state; and (4) the branching ratio for the production of $C_2H_3^+$ and $C_2H_2^+$ is the same.

3. Conclusions

We have proposed a mechanism for the fragmentation of ethylene interacting with a strong Ti:sapphire laser pulse. According to this model the dissociation of the molecules is the result of MPI of the inner-valence electrons which results in a molecular ion in an excited state. Through radiation-less transition, the population is transferred to the highly excited levels of the ground electronic state. The molecular ion created in this manner is unstable and dissociates rapidly. The model was tested by comparing the measured laser-intensity-dependent abundance of two fragments ($C_2H_3^+$ and $C_2H_2^+$) with the calculated ones and excellent agreement was obtained with the experimental results.

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