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Analysis of femtosecond laser ionization/dissociation of polyatomic molecule $C_6H_{10}O$ from one-colour pump–probe measurement*

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This paper reports that a one-colour fs pump–probe measurement has been carried out for studying photoionization/photodissociation of cyclohexanone ($C_6H_{10}O$) in intense laser field. Two of the fragments from cyclohexanone, $C_2H_3^+$ and $C_3H_3^+$, are studied under 800 nm laser pump–probe and the results obtained show similar time evolutions. It proposes a feasible model for analysing the experimental observations of the one-colour fs pump–probe measurement. The results demonstrate that as an intermediate product, the excited molecular parent ions play a very important role in photionization/photodissociation processes in intense laser field.

Keywords: cyclohexanone, fs pump–probe, ionization/dissociation
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Femtosecond (fs) pump–probe technique has been employed widely for exploring the dynamics in molecular ionization/dissociation.[1] In general, two laser beams with different colours are necessary for monitoring the evolution of molecular wavepackets and elucidating the decay times of molecular excited states involved in the processes since different colour laser beam can be used as pump or probe for selecting a specific intermediate state or channel for studying.[2–8] Pump–probe experiment is also carried out sometime with one-colour laser by splitting it into two beams.[9,10] These one-colour fs laser pump–probe methods are simple experimentally but bring with a difficulty for explaining the results of measurement due to the identity between the pump and probe beams. In this work, we carry out a one-colour fs laser pump–probe experiment of cyclohexanone molecule ionization/dissociation in a laser field intensity of $10^{13} \sim 10^{14}\,\mathrm{W/cm^2}$ and develop an analytical method for the observed decays of molecular fragment ions. The results demonstrate that this method provides a feasible way for explaining the one-colour fs pump–probe experiment and obtaining the information of pathways on ionization/dissociation of polyatomic molecules in fs laser field.

The ionization/dissociation of cyclohexanone ($C_6H_{10}O$) under fs laser field have been reported in recent years by several groups. Kosmidis *et al* studied the forming mechanism of the multi-charged cyclohexanone ion[11] and their Coulomb explosion[12] under 790 and 395 nm fs laser radiation with intensity of 10^{14}–$10^{16}\,\mathrm{W/cm^2}$. Wu *et al* measured the ionization efficiency of cyclohexanone with 800 nm, 50 fs laser in the intensity range of 5–$13\times10^{13}\,\mathrm{W/cm^2}$ and observed that fragmentation of parent ions increases with increasing molecular size, and explained it with a non-statistical mechanism.[13] A significant resonant effect of the cation photoabsorption on ionization and dissociation of cyclohexanone molecules was found in our previous study with a 90 fs 788 or 394 nm laser field ranging from $5\times10^{13}\,\mathrm{W/cm^2}$ to $2\times10^{14}\ \mathrm{W/cm^2}$.[14] For time-resolved studies, a pioneering work was done by Zewail's group in which the time for CO dissociation from different sized cycloketone molecules was found to be in the range of 100–200 fs and increases with increasing number of atoms.[15]

Our experimental observation on cyclohexanone ionization/dissociation was carried out with a lin-

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ear time-of-flight mass spectrometer. A 90 fs 800 nm laser beam was generated from a Ti:Sapphire laser (Spectra-Physics). This laser beam was split into two parts as a pump and a probe beam with the fixed intensity ratio $I_{\rm pump} : I_{\rm probe}$=1.3:1 approximately. A time delay between two beams was realized by putting a translation stage (Zolix Instruments Co., Ltd.) into the path of the probe beam. These two beams were recombined after the stage and intersected with a molecular beam from a pulsed valve with a backing pressure of 5 Torr (1 Torr=133 Pa), the saturated vapour pressure of cyclohexanone at room temperature, in a vacuum chamber. The produced ions were extracted and accelerated by electric fields normal to laser-molecule beam plane and detected after 1 m field-free flight in the mass spectrometer.

Figure 1 shows the typical mass spectra obtained with a pump beam only, a probe beam only, and two beams together but different delay times (0 and 1.5 ps), respectively. The laser intensity at the focus for zero time delay used here is 1.75×10^{14} W/cm^2. Under this intensity, the parent $C_6H_{10}O^+$ (m/e=98) and some fragment ions, mainly $C_2H_m^+$ ($m = 0-5$) and $C_3H_n^+$ ($n = 0-6$), can be observed even though only a pump or a probe beam was used. All peak intensities of the parent and the fragments increase significantly when two beams with a zero delay time are used. In all mass spectra, besides the parent ion, $C_2H_3^+$ ($m/e = 27$) and $C_3H_3^+$ ($m/e = 39$) are the next predominant ions and their intensities change with the time delay between the pump and probe beams. The formation of these ions are attributed to a primary ionization process of the polyatomic molecule (quasiresonant process),[14] followed by some decay processes from the excited parent ion $C_6H_{10}O^+$ produced further by the fs laser field. As it is known, in an intense laser field, multiphoton ionization or field ionization can occur within one laser pulse duration.[14,16,17] Therefore, the excited $C_6H_{10}O^+$ as the intermediate plays an important role to determine the experimental observations and a time resolved measurement is also necessary to explore its dynamical process.

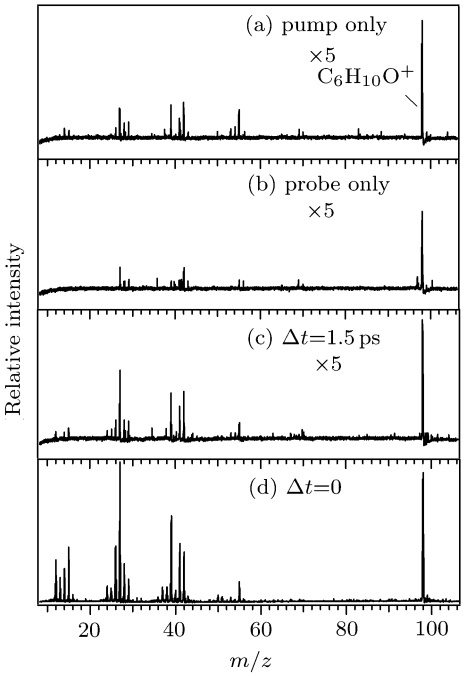


Fig.1. Mass spectra of $C_6H_{10}O$ at the laser intensity of 1.75×10^{14} W/cm^2 at the focus for zero time delay (here the ratio $I_{\rm pump} : I_{\rm probe}$ is 1.3:1). The groups of the fragment ions are CH_n^+ ($n = 0-3$), $C_2H_n^+$ ($n = 0-5$), and $C_3H_n^+$ ($n = 0-6$), respectively, in the mass spectra from the left to right.

The ion intensities as a function of the pump–probe delay Δt were measured. The results of fragments $C_2H_3^+$ and $C_3H_3^+$ under different laser intensities from 1.75×10^{14} to 5.01×10^{14} W/cm^2 are shown in Fig.2. For the lowest laser intensity, the curves are symmetric and have the maximum at the zero delay

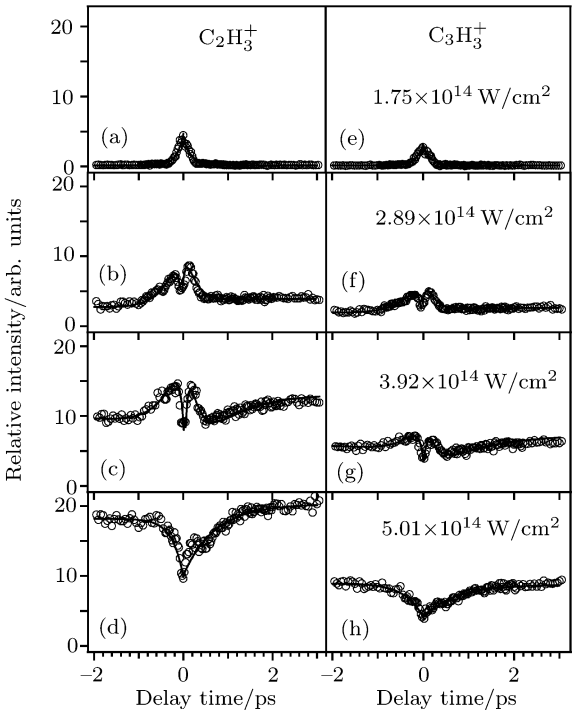


Fig.2. Experimental pump–probe curves (as shown in circles) of $C_2H_3^+$ under different laser intensities: (a) and (e) 1.75×10^{14}; (b) and (f) 2.89×10^{14}; (c) and (g) 3.92×10^{14}; (d) and (h) 5.01×10^{14} W/cm^2. The best fit (as shown in solid lines) parameters used are given in Table 1 for each subfigure from (a) to (h). In our experiments, $I_1 < I_2$ when $\Delta t < 0$.

time. With increasing laser intensity at different delay times all the curve raises gradually, due to the enough laser intensity for generating the products by one laser beam. A dip appears and develops near the position of the zero delay time, and the ion signals are at the minimum at this zero delay time when the laser intensity reaches the maximum.

To explain the experimental results, we propose a simple model with two pathways of molecular ionization/dissociation according to the relaxation of its intermediate involved in the pump–probe scheme (Fig.3). If the relaxation with a time constant τ_1 is relatively large, the molecular intermediate (i), produced by the first laser pulse from the ground-state molecule (g), can be excited further by the second laser pulse with a certain delay time to a final state (f), and then the molecule dissociates from the f state into the product D^+ that is observed experimentally, as shown in Fig.3(a). However, if the intermediate relaxes fast into another intermediate (j), further excitation by the second laser pulse will be from the j state to the final state f which dissociates finally into the product D^+ observed, as shown in Fig.3(b). The probability of the observed product D^+ in each case is related with the excitation and relaxation of the intermediate. In case 1, the production probability of the product D^+, P_1 and P_1' in the region of $\Delta t < 0$ and $\Delta t > 0$ can be written respectively as follows:

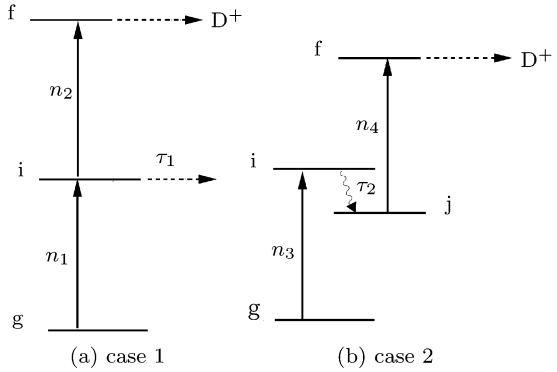


Fig.3. Two cases for polyatomic molecule's ionization / dissociation into fragments.

$$P_1 = \sum_{i=1}^{n} \exp(\Delta t/\tau_{1i}) \times \int_{-\infty}^{+\infty} \sigma_{n_{1i}} \cdot I_1^{n_{1i}}(t_1)\mathrm{d}t_1 \times \int_{-\infty}^{+\infty} \sigma_{n_{2i}} \cdot I_2^{n_{2i}}(t_2)\mathrm{d}t_2 + c_1 \quad \text{for} \quad \Delta t < 0, \tag{1}$$

$$P_1' = \sum_{i=1}^{n} \exp(-\Delta t/\tau_{1i}') \times \int_{-\infty}^{+\infty} \sigma_{n_{1i}} \cdot I_2^{n_{1i}}(t_1)\mathrm{d}t_1 \times \int_{-\infty}^{+\infty} \sigma_{n_{2i}} \cdot I_1^{n_{2i}}(t_2)\mathrm{d}t_2 + c_1' \quad \text{for} \quad \Delta t > 0, \tag{2}$$

where Δt is the delay time between two laser pulses, τ_{1i} and τ_{1i}' are the time constants of relaxation of corresponding intermediates for $\Delta t < 0$ and $\Delta t > 0$, respectively; since the intermediate can be different for different time region, n_{1i}, and n_{1i}' are the laser intensity indices, and $\sigma_{n_{1i}}$ and $\sigma_{n_{1i}}'$ are the cross sections for multiphoton excitation processes. The sum is for different intermediates involved in the processes. Since two laser beams are identical, their intensities are related by

$$I_1(t) = k \cdot I_2(t). \tag{3}$$

When the beam with the intensity I_2 is fixed and another beam, I_1, is moved relative to the fixed beam, and thus, $\Delta t < 0$ means that the beam I_1 comes earlier than the beam I_2. In this case, for $k < 1$, the weak beam I_1 interacts with molecules earlier. Since all integrals in Eqs.(1) and (2) denote some probabilities of the processes and they can be considered as the parameters, equations (1) and (2) then reduce to the simple forms

$$P_1 = \sum_{i=1}^{n} M_i \cdot \exp(\Delta t/\tau_{1i}) + c_1 \quad \text{for} \quad \Delta t < 0, M < 1, \tag{4}$$

$$P_1' = \sum_{i=1}^{n} M_i' \cdot \exp(-\Delta t/\tau_{1i}') + c_1' \quad \text{for} \quad \Delta t > 0, M' < 1. \tag{5}$$

Similarly, for the case 2, we have

$$P_2 = \sum_{i=1}^{n} (1 - \exp(\Delta t/\tau_{2i})) \cdot \int_{-\infty}^{+\infty} \sigma_{n_{3i}} \cdot I_1^{n_{3i}}(t_1)\mathrm{d}t_1 \times \int_{-\infty}^{+\infty} \sigma_{n_{4i}} \cdot I_2^{n_{4i}}(t_2)\mathrm{d}t_2 + c_2$$
$$= \sum_{i=1}^{n} N_i \cdot (1 - \exp(\Delta t/\tau_{2i})) + c_2, \quad \text{for} \quad \Delta t < 0, N \leq 1, \tag{6}$$

$$P_2' = \sum_{i=1}^{n} (1 - \exp(-\Delta t/\tau_{2i})) \cdot \int_{-\infty}^{+\infty} \sigma_{n_{3i}} \cdot I_2^{n_{3i}}(t_1)\mathrm{d}t_1 \times \int_{-\infty}^{+\infty} \sigma_{n_{4i}} \cdot I_1^{n_{4i}}(t_2)\mathrm{d}t_2 + c_2'$$
$$= \sum_{i=1}^{n} N_i' \cdot (1 - \exp(-\Delta t/\tau_{2i}')) + c_2' \quad \text{for} \quad \Delta t > 0, N' \leq 1. \tag{7}$$

By using these equations, we can obtain numerical results for the cases 1 and 2. The production probabilities as a function of the delay time Δt show quite different trends for different time constants of the intermediate, as shown in Fig.4. For example, at the time with a zero delay, the production probability reaches a maximum for the case 1 but a minimum for the case 2. This obvious difference can be taken as a criterion for judging whether the observation is produced through an intermediate with fast or slow relaxation. Next, the time constant τ of the relaxation from the state i has a great influence on the shape of the production probability as a function of the two laser-beam delay time. If τ is long enough (e.g. 1 ps), the production probability varies gradually with the delay time $|\Delta t|$. However, if τ is shorter (e.g. 100 fs) a sudden change in the vicinity of the delay time $|\Delta t| = 0$ will show up.

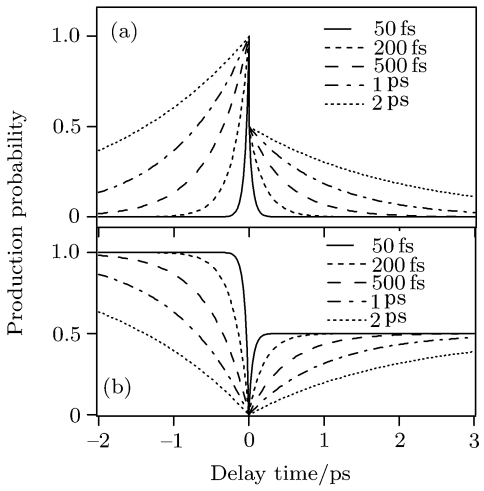


Fig.4. The variety of production probability (PP) of a given fragment with the delay time under the different time constant of relaxation of i. Figure (a) corresponds to case 1. Here, $M = 1$, and $M' = 0.5$. Figure (b) corresponds to case 2. Here, $N = 1$, and $N' = 0.5$.

The numerical simulation for the experimental measurements are carried out by using Eqs.(4) and (5) or Eqs.(6) and (7) for the different cases under low and high laser intensity, respectively. In fact, the situations for the intermediate laser intensities, 2.89×10^{14} and $3.92\times10^{14}\,\mathrm{W/cm^2}$, are complex because of the competition of two processes. All simulation results are shown by the solid lines in Fig.2 and the time constants obtained are given in Table 1.

From the previous studies, we consider that the intermediate is the excited-state parent ion produced by photoionization of neutral cyclohexanone in intense laser field, just as mentioned above, and the same intermediate is involved within the used laser intensity region. This also implies that the intermediates for both cases 1 and 2 should be the same. Thus, some useful information on photodissociation dynamics of cyclohexanone in intense laser field can be obtained by comparing these stimulating results and the experimental result for one-colour fs pump–probe. Firstly, Table 1 shows that the time constants obtained for $C_2H_3^+$ and $C_3H_3^+$ are roughly the same at a given laser intensity. This similarity indicates that these two fragments most probably come from same precursors of which the pathways can be complicated (e.g., α bond breakage, H transfer, and several sequential dissociation). But the producing rates are determined by the same intermediate, the excited parent ion from photoionization.[14] $C_2H_3^+$ and $C_3H_3^+$ are produced in strong laser field from this precursor. Secondly, with the increase of the laser intensity, τ_1 increases and τ_2 decreases. Therefore, it is believed that under low laser intensity the excited parent ions may not have enough internal energy for further α bond breakage, H transfer, and so on. They decay mainly through a pro-

cess, such as a fast internal conversion or intramolecular vibrational relaxation, whose rate decreases with the increase of laser intensity for reasons such as a modification of the potential energy surfaces by the nonresonant laser field,[18] for example. It is possible that the dressed potential of the excited parent ion between two avoided crossings has a minimum which acts as a light induced well in which the parent ion may be trapped from further dissociation. For high laser intensity, the excited parent ion may absorb more photons and suffer a further dissociation sooner through α bond breakage and H transfer. Obviously, the rate of this process is increased with the increase of laser intensity, leading to a decreased τ_2.

Table 1. Time constants of relaxation of $C_2H_3^+$ and $C_3H_3^+$ under different laser intensities.

Intensity/(W/cm^2)	$C_2H_3^+$ ($m/e = 27$)				$C_3H_3^+$ ($m/e = 39$)			
	$\Delta t < 0$		$\Delta t > 0$		$\Delta t < 0$		$\Delta t > 0$	
	τ_1/ps	τ_2/ps	τ_1'/ps	τ_2'/ps	τ_1/ps	τ_2/ps	τ_1'/ps	τ_2'/ps
1.75×10^{14}	0.15		0.17		0.15		0.17	
2.89×10^{14}	0.45	1.2	0.2	1.0	0.45	1.0	0.19	1.5
3.92×10^{14}	0.6	0.9	0.25	0.8	0.5	0.8	0.3	1.1
5.01×10^{14}		0.25		0.7		0.4		0.7

It should be noted that in our model the decay processes of the neutral molecule are omitted since, as mentioned before, the neutral molecule is believed to be ionized primarily when exploring in the fs-laser field. The formation of the final states from the intermediates by the second laser beam is dominative. These effects such as interference or coherence between different channels when the two beams overlapped in time are also negligible. These assure some validity of the model for analysing complex molecular processes in an fs-laser field.

In conclusion, we have performed a one-colour fs pump–probe measurement of cyclohexanone in intense laser field. The experimental observations are interpreted by a proposed simple model. The results demonstrate that as an intermediate product, the excited molecular parent ions play a very important role in photionization/photodissociation processes in intense laser field. The analysis used here may be useful in further one-colour pump–probe studies on photodissociation dynamics of polyatomic molecules.

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