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Fragmentation of dimethyl ether in femtosecond intense field

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Abstract

The fragmentation of dimethyl ether (DME) in intense femtosecond laser field has been studied at 810, 405 and 270 nm with intensities up to 2.48×10^{15}, 3.86×10^{15} and 1.62×10^{14} W/cm^2, respectively. At 405 nm, DME is possibly firstly ionized by multiphoton absorption, and then parent ion DME^+ dissociates into fragments via filed-induced dissociation. For 810 and 270 nm laser fields, DME firstly dissociates into CH_3O and CH_3 fragments and then these neutral fragments are ionized by field tunneling. Another possible way for DME to dissociate at 810 and 270 nm is that DME is ionized by intense field ejection of inner valance electron and then the excited DME^+ dissociates into fragment ions. Ultrafast rearrangement of DME or DME^+ in intense field may be responsible to the unpredictable fragment ions, $CHO^+/C_2H_5^+$ and H_2^+.

Keywords: Fragmentation; Dimethyl ether; femtosecond intense field

1. Introduction

It has been found that with femtosecond laser ionization, fragmentation was much less than with nanosecond pulses in many molecules [1–8], which was a great advantage in mass spectroscopy for analytical purposes. However, there are also some reports that molecules under femtosecond irradiation, such as saturated hydrocarbons, showed extensive fragmentation, without any parent ions [9,10].

For atoms in intense field, the transition between the multiphoton ionization (MPI) and field tunneling ionization (FI) regimes can be distinguished according to adiabaticity parameter γ, proposed by Keldysh [11]:

$$\gamma = \sqrt{\mathrm{IP}/(1.87 \times 10^{-13} \times I_0 \times \lambda^2)} \quad (1)$$

where IP is the ionization potential (eV) in the absence of the laser field, I_0 is the peak intensity (W/cm^2) and λ is the laser wavelength (μm). $\gamma < 1$ implied the participation of an FI mechanism, while $\gamma > 1$ the ionization was attributed to MPI process. Keldysh model has been widely applied to explain molecules behaviors in intense field. However, γ is only determined by λ and IP, which is not valid in many cases, even for diatomic molecule. For example, O_2 [12], observation showed significant discrepancies between experiment and theory. Even for $\gamma > 3$, ionization of benzene was attributed to FI [13]. The abundance of parent ion was suggested to be influenced by ionic state resonances [6,14]. However, opposite observation was also reported that the parent ion might be not affected by resonances with ionic states [15].

Controls of the molecular fragmentation in intense field are interesting phenomena [16,17], which require thorough understanding of the interaction mechanism between the molecular system and the laser beam. Ionization/dissociation mechanism in the intermediate range (10^{13}–10^{15} W/cm^2) is still less clear. Fragmentation of molecules in intense laser field has often been interpreted by two types of models: one-step model and several-step model. One-step model suggested that fragmentation and ionization occurred in a same process, and correlations of the two were related with properties of neutral molecule, such as

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electronic structures [13] and bond lengths [18]. Another one-step model suggested that high-intensity laser ionized lower-lying orbital, giving rise to an electronically excited ion, which then dissociated into fragment ion [19]. In two-step model, excitation and photodissociation followed ionization of the parent molecules [6,14,20,21,24], and resonances of the parent ion with laser excitation played a key role in the second step. The importance of ionic resonances was recently discussed in the case of polycyclic aromatics [15]. Another multi-step model, re-collision model, suggested that the primary parent ion collided with the oscillating free electrons [22,23].

Dimethyl ether (DME) is a simple but very important organic molecule. Dissociation dynamics of DME has been studied extensively [25–33]. In nanosecond REMPI experiment [34], DME was ionized, at first, via three-photon excitation and fourth photon ionization, and followed by dissociation into charged species, CH_3^+ and $CHnO^+$ ($n = 1$–3).

Here, we report our experimental investigations on fragmentation process of DME in 60 fs intense optical field at three wavelengths, 810, 405 and 270 nm, respectively. For this simple organic molecular, several unusual fragment ions are observed, such as $CH_3OCH_2^+$, $CHO^+/C_2H_5^+$ and H_2^+. The extents of fragmentation of DME in intense laser field are dependent on both wavelengths and intensities.

2. Experiment

The experimental setup has been described elsewhere [35]. Briefly, the self-mode-lock Ti:sapphire laser oscillator, pumped by a 5 W 532 nm laser (Verdi-5, Coherent Inc.), produces the seed pulses at a repetition of 110 MHz, centered at 800 nm with about 40 fs pulse duration. After compression, the solid-state femtosecond laser system outputs 800 nm fundamental pulses (with ~50 nm bandwidth) at 20 Hz repetition rate with 60 fs width and 160 mW average power. Pulse width is determined by single-shot intensity autocorrelation method. The fundamental light is frequency doubled by a β-BaB_2O_4 crystal (BBO, type I) to produce second harmonic generation (SHG), centered at 400 nm. For 270 nm light, the SHG and residual fundamental light are combined together to generate the third harmonic generation (THG) light centered at about 270 nm by an additional BBO crystal (Type II).

The fundamental light, SHG and THG beams are focused by a 30 cm fused quartz lens into the chamber of a TOF mass spectrometer. The laser intensities at the focus spot could be varied by using different neutral density attenuators.

The time of flight mass spectrometer is a typical Wiley–McLaren machine. Sample gas, 5% dimethyl ether (DME) in He, is expanded through a pulsed valve (general valve, with 0.5 mm orifice), into the ionization accelerating region, 5 cm downstream from the nozzle. Ions in this region are extracted and accelerated by a typical three electrodes system, and detected by a two-stage microchannel plate (MCP) detector at the end of the flight tube. Output of MCP is fed into a digital oscilloscope (Tektronix Inc., TDS3054B), GPIB interfaced with a computer. Each TOF mass spectrum is the average result over 532 laser shots. With molecular beam on, the source chamber and flight chamber are maintained at 1.5×10^{-4} and 6×10^{-6} Pa, respectively.

3. Result and discussions

Fig. 1 illustrates the typical TOF mass spectra of DME at three wavelengths, respectively. In order to compare the mass spectra in these three cases, all the spectra are normalized. Interesting phenomena in Fig. 1 are evident: (1) dramatically change of DME^+/CH_3^+ ratio from 810 to 270 nm; (2) different fragment patterns; (3) great change of relative yields of H^+ and H_2^+ to DME^+ from 810 to 270 nm; (4) similar intensity of $CH_3OCH_2^+$ to that of DME^+. No detectable dimmer is observed.

In nanosecond experiments [34], DME was first ionized, followed by fragmentation to charged products in the wavelength range of 450–550 nm. Main charged fragments of the following dissociation channels were observed:

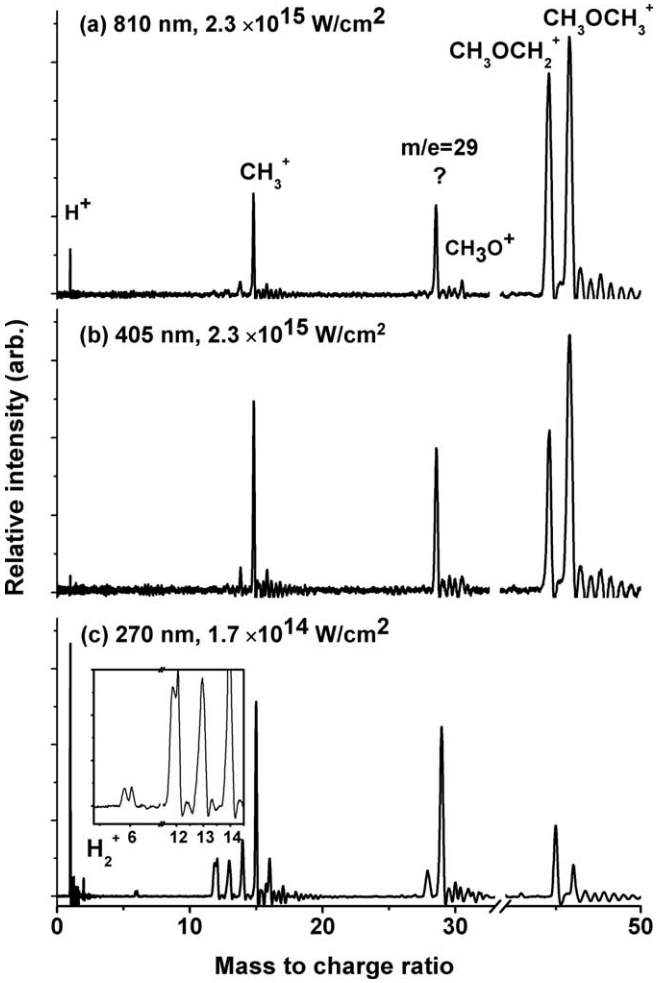

Fig. 1. Typical TOF mass spectra of DME at three wavelengths.