

Chirping-dependent ionization and dissociation of methane in an intense femtosecond laser field

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We studied the ionization and dissociation of polyatomic molecule methane in an intense femtosecond laser field with wavelength of 810 nm and intensities ranging from 1.4×10^{14} to 2.6×10^{15} W/cm² by mass spectroscopy. Abundant fragment ions were observed in addition to the strong parent ion. The effect of frequency chirp was investigated and it was found that the negatively chirped pulses dramatically enhanced the dissociation probability, which might be used to control the dissociation pathways.

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Over the last several years, much attention has been paid to the ionization and dissociation of molecules in an intense laser field as the electric field of the laser approaches or even surpasses the binding field of the valence electrons^[1-5]. When such a strong oscillatory field interacts with molecules, the interaction between the molecule and the laser field cannot be treated in a perturbative manner. In general, the interaction of intense radiation fields with molecules can result in both electron emission and subsequent dissociation. There are two regimes in the coupling of intense radiation fields with polyatomic molecules. One is the multiphoton regime in which n photons couples simultaneously into the molecule to allow excitation to intermediate electronic state or directly to an ionic state. The other regime for radiation-molecule coupling involves the production of field ionization via tunneling or barrier suppression. For a variety of molecules interacting with intense femtosecond laser pulse, intact parent ion was observed in addition to the dissociation fragments^[2-5]. The dissociation pathway is complex and hard to be controlled, although the controlling of chemical reaction product using laser has great significance in synthesizing chemical substances with high efficiency^[6-10]. Many chemical reactions follow more than one reaction pathway, each leading to a different product. Usually, only one of these pathways is desired for the selected reaction. The primary goal of practical chemistry is to produce desired molecule products with substantial yield. For decades, enhanced productivity was attained by thermodynamic techniques, e.g. variations in pressure and temperature. Recently, efforts have been directed toward using properties of laser. For example, tailored ultrashort chirped pulses have been emerged as a powerful tool for quantum control of reactions by selectively breaking and making chemical bonds in polyatomic molecules^[9-13].

In this paper, we focus our attention on the ionization and dissociation of methane in an intense femtosecond laser beam with duration of 110 fs and wavelength centered at 810 nm. We measured the time-of-flight (TOF) mass spectra for the laser intensity range from 1×10^{14} to 3×10^{15} W/cm². Moreover, the dissociation branching ratios at different chirp and pulse duration were also measured. We found that the negatively chirped pulses can significantly enhance the dissociation probability.

The experimental setup is shown in Fig. 1, which has been described previously^[14]. A Ti:Sapphire chirped pulse amplifier (CPA) laser system (TSA-10, Spectra-Physics Inc., USA) with a repetition rate of 10 Hz was employed as the light source. The final chirp-free autocorrelated pulse duration full width at half maximum (FWHM) was measured to be 110 fs (Fig. 2). By varying

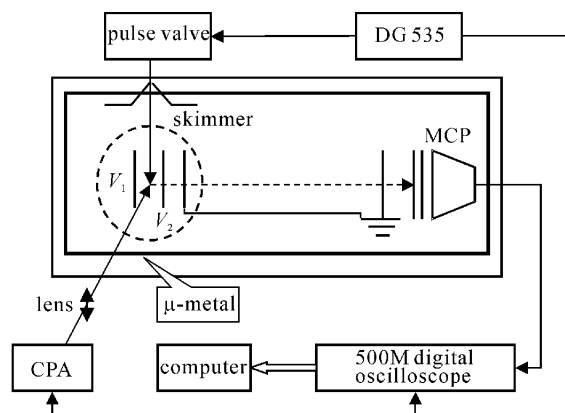


Fig. 1. Schematic diagram of the home-made TOF mass and photoelectron spectrometer. The timing schedules of the general pulsed valve, CPA laser and the sampling oscilloscope were controlled by a DG 535 digital delay.

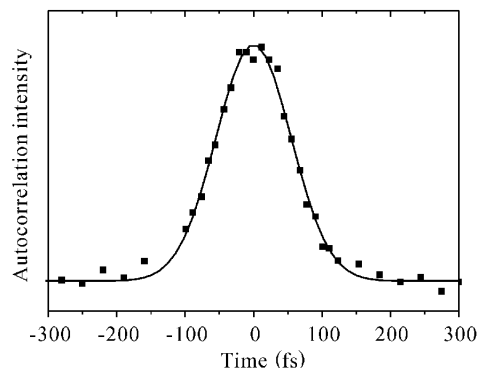


Fig. 2. Single-shot autocorrelation trace of the 110-fs (FWHM) laser pulse. A Gauss fit was made to fit the experimental data.

the displacement of the grating in the laser system, the optical path between different frequency components in the laser pulse can be changed. This will alter the chirp of laser pulse as well as the pulse duration. The pulse duration was monitored by a single-shot autocorrelator (Positive Light). The laser energy was measured with a powermeter (Rj 7200 series radiometer, Laser Precision Corp., USA) and the maximum output is 10 mJ per pulse. The amplified laser beam was focused into the chamber of the TOF mass spectrometer with a lens of 150-mm focal length. The inner-wall of the entire vacuum chamber was wrapped with μ -metal to shield the geomagnetism. The gaseous methane was introduced into the chamber via a pulsed valve (Park Inc., USA) with a 0.2-mm orifice. The chamber pressure was maintained at several 10^{-4} Pa to avoid space-charge effect and pressure broadening of the ion peaks. This system employed a dual slope extraction field. The distance between V1 and V2 plates was 10 mm. The charged particles were extracted to the field-free drift tube of 35-cm length. A micro-channel plate assembly was used to detect the ions or photoelectrons. The signals were recorded using a digital oscilloscope with a 500-MHz sampling rate (H-P, USA) and were typically averaged over 256 times. The data were then transferred to a PC for storage and analysis.

Figure 3 shows the TOF mass spectra of methane irradiated by 810-nm, 110-fs laser pulses at intensities ranging from 1.4×10^{14} to 2.6×10^{15} W/cm². The signals H₂O⁺, O⁺ and O²⁺ were originated from the residual water in the vacuum chamber. Abundant signals of fragment ions H⁺, C^{m+} ($m=1, 2, 3$) and CH_{*n*}⁺ ($n=1, 2, 3$) in addition to the parent ion CH₄⁺ were observed at the highest laser intensity. In the figure, all the ion signals in the mass spectra decrease with decreasing laser intensity. We can hardly see any obvious ion signal when the laser intensity is lowered to 1.4×10^{14} W/cm². The Keldysh parameter $\gamma = \sqrt{|IP|/(2U_p)}$ (0.84 – 0.20) is less than unit in our experiment where U_p is the ponderomotive potential of an electron in the laser field and IP is ionization potential of the molecule. This indicates

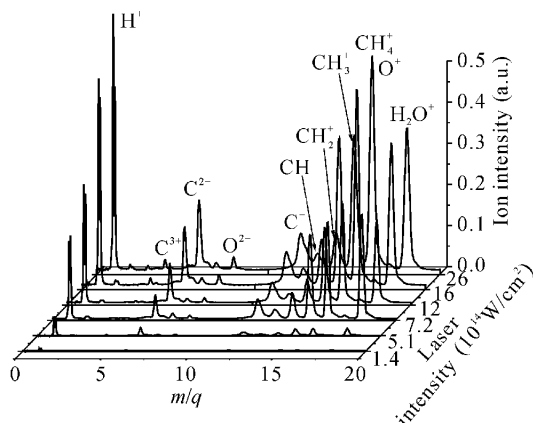


Fig. 3. TOF mass spectra for methane excited using 810-nm, 110-fs laser pulses as a function of laser intensity from 1.4×10^{14} to 2.6×10^{15} W/cm². The extraction voltages of V1 and V2 plates are 960 and 800 V, respectively. The signals H₂O⁺, O⁺ and O²⁺ originated from a background gas.

that the field ionization domains under our experiment conditions.

Figure 4 shows the variation of ions CH_{*n*}⁺ ($n = 0 - 4$) with the laser intensity. It was noted that these singly charged fragmental ions had a similar dependence on laser intensity as the molecular ion CH₄⁺. We have concluded that the observed singly charged fragmental ions CH₃⁺, CH₂⁺, CH⁺ and C⁺ are originated from the rapid dissociation of the highly excited molecular ions that were produced through ionization of the inner-valence electrons^[15].

By varying the displacement of the grating in the laser system, we can change the chirp of the laser pulse. We defined the yield branching ratio by fragment ion yield over parent ion yield to express the dissociation channels. Figure 5 depicts the variation of CH₃⁺/CH₄⁺ and CH⁺/CH₄⁺ versus chirp. By comparing the negative chirp and positive chirp, we can see that the negatively chirped pulses can significantly enhance the dissociation probability which agrees with previous theoretical work^[16,17]. As for the increasing of yield branching ratio with positive chirp, we contribute it merely to the duration effect that longer pulse duration can induce higher degree of fragmentation^[18,19].

The experimental result can be interpreted as follows.

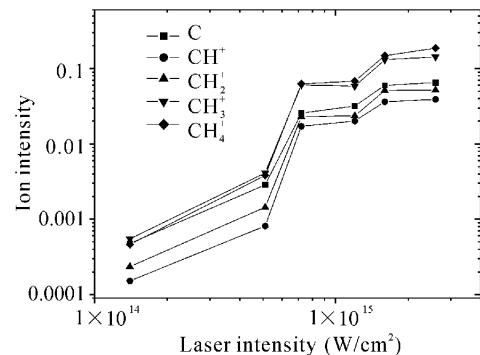


Fig. 4. The ion intensity of CH_{*n*}⁺ ($n = 0 - 4$) as a function of laser intensity. It can be seen that these singly charged fragment ions have a similar dependence on laser intensity compared with the parent ion.

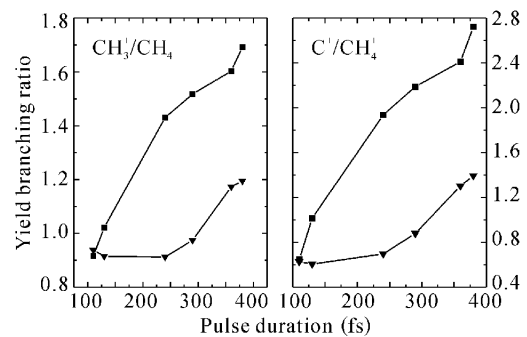


Fig. 5. The yield branching ratio of CH₃⁺ (left) and C⁺ (right) at different pulse duration with positive chirp (triangles) and negative chirp (squares). The negatively chirped pulses can greatly enhance the dissociation probability. We contribute the increase of yield branching ratio for positive chirp to the duration effect.

The potential energy surface (PES) of a molecule, whose shape is determined by its electronic configuration, could be deformed in intense laser fields. The newly formed PES is called light-dressed PES, that is, PES wearing a dress of light^[20]. A molecule system is characterized by the PES on which wave packets propagate. By controlling the direction of nuclear motion on the PES, the nuclear motion leads to breaking of a specific chemical bond. The pulse can be tailored to drive a molecular state to a target on its potential energy surface and then steer it toward a channel that favors a particular photochemical outcome. In our experiment, the femtosecond linear chirped pulses were used. In general, the energy level spacing of molecule vibrational states decreases from lower to higher states. A negatively chirped pulse (frequency components shift in time from blue to red) might maintain resonance with the wave packet as it evolves along the excited states surface, which is called the ladder-climbing mechanism^[16]. In contrast, a positively chirped pulse might quickly go off resonance with the wave packet, and the photoexcitation would be non-selective.

In conclusion, the interaction of methane molecule with an intense femtosecond laser pulse was presented. The observed singly charged fragmental ions are believed to be originated from the rapid dissociation of the highly excited molecular ions. We also studied the effect of frequency chirping on dissociation channels and demonstrated that a linear negatively chirped pulse can more efficiently excite molecule from low-energy to highly excited states than a positively chirped pulse does. This offers a way to control the chemical reaction by selectively breaking or making chemical bonds.

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