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Dissociative ionization of methanol in medium intense femtosecond laser field using time-of-flight mass spectrometry

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HIGHLIGHTS

- Dissociation follows step-wise dissociation with no sign for Coulomb explosion.
- CH_3OH^+, $CH_3O^{+\cdot}$ CH_3^+ form at 1.4×10^{13}, 1.7×10^{13}, 2.0×10^{13} W/cm^2, respectively.
- C^+, CH^+, CH_2^+, OH^+, and O^+ and the H^+ is detected at $2.8*10^{13}$ W/cm^2.
- H_2^+ is detected at 3.0×10^{13} W/cm^2.
- Among all ions, only H^+ was found to have angular anisotropic distribution.

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ABSTRACT

800 nm 100 fs laser combined with TOF mass spectrometer was used to investigate the dissociative ionization of methanol, CH_3OH in the laser intensity less than 4×10^{13} W/cm^2. The results showed that the dissociation follows a sequential step-wise dissociation pattern, with no sign for Coulomb explosion. At very low intensity 1.4×10^{13} W/cm^2, only the parent ion CH_3OH^+ appears. At 1.7×10^{13} W/cm^2, the dissociation products are mainly due to hydrogen elimination from the O–H or C–H bonds forming CH_3O^+ and CH_2OH^+ primary ions. At 2.0×10^{13} W/cm^2, the C–O bond starts to break forming CH_3^+, which simultaneously dissociates to CH_2^+. The primary fragment ions CH_3O^+ and CH_2OH^+ start to dissociate into lower secondary fragments as CH_2O^+ and CHO^+ for the former and $CHOH^+$ and COH^+ for the latter. At 2.8×10^{13} W/cm^2, secondary dissociation fragments dominate the spectrum including C^+, CH^+, CH_2^+, OH^+, and O^+ and the H^+ is detected. At 3.0×10^{13} W/cm^2, H_2^+ is detected. For all ions formed, the ion yield increases with laser intensity till it reaches maximum, after which it drops down manifesting the dissociation of these ions into smaller fragments. Among all ions, only H^+ was found to have angular anisotropic distribution.

1. Introduction

Intense laser fields generated from ultrashort laser pulses have a remarkable impact on our understanding of new phenomena in chemical and physical science. Focusing of these intense laser light pulses can generate peak intensities higher than 10^{15} W/cm^2. Therefore, laser electric field of such a magnitude becomes comparable to the Coulomb field which binds valence electrons to the nucleus. Accordingly, various physical phenomena, including multiphoton ionization (MPI) (Bandrauk, 1994), dissociative ionization (Bandrauk, 1994; Codling and Frasinski, 1993; Corkum and Dietrich, 1993; Guisti-Suzor et al., 1995; Ilkov et al., 1995), field ionization (Dewitt and Levis, 1998; Wu et al., 2001), Coulomb explosion (Ellert et al., 1998; Iwamae et al., 2000; Chelkowski and Bandrauk, 1995; Ledingham et al., 1999; Kamta and Bandrauk, 2005) and field assisted dissociation (Tang et al., 2003; Wang et al., 2003; Elshakre et al., 2003) can result. To investigate the dynamical behavior of polyatomic molecules in intense laser fields, various studies were carried out at laser intensities higher than 10^{14} W/cm^2 (Cornaggia, 2000; Hering, 1998; Cornaggia et al., 1992', 1996; Safvan et al., 1998; Banerjee et al., 1999; Castillejo et al., 1998', 1999; Smith et al., 1998; Kosmidis et al., 1997). It is not straightforward to interpret and to offer a plausible explanation of the dissociation and ionization mechanisms of the experimental data at such high intensities. One of the widely adopted mechanisms is the Coulomb explosion mechanism, where multiply charged ions are formed, which subsequently undergo electrostatic repulsions leading to their dissociation (Cornaggia, 2000; Hering, 1998; Cornaggia et al., 1992; Wu et al., 2002; Furukawa

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et al., 2005; Okino et al., 2006). It is the objective of this work to investigate the dissociative ionization of methanol at medium intensities of 10^{13}–10^{14} W/cm^2, lower than 10^{15} W/cm^2, by addressing the step-wise dissociation mechanism, where only singly charged ions are formed. In this mechanism, the laser intensities generated from 100 fs femtosecond pulses gradually and stepwisely increase while the results of dissociative ionization as a function of laser intensity are monitored.

Methanol is a polyatomic molecule that has three various types of bonds; C–H, C–O, and O–H bonds. It is interesting to demonstrate how these various bonds respond to intense electric field of 10^{13}–10^{14} W/cm^2. Experimentally, the dissociation of methanol in high laser intensity in the range of 6×10^{13} W/cm^2–3×10^{15} W/cm^2 was investigated by Wu et al. (2002) who observed singly and multiply charged fragmented ions, where the appearance of the charged ions were explained on the basis of Coulomb explosion. Yamanouchi and coworkers (Furukawa et al., 2005; Okino et al., 2006) found that H_3^+ ion is ejected from methanol molecule via two-body Coulomb explosion at laser intensity of 10^{14} W/cm^2. On the other hand, Ueda et al. (Hatamoto et al., 2007) studied the dissociative ionization of methanol in a moderate intense laser field 10^{12}–10^{13} W/cm^2, considering only MPI as the only process involved to interpret their results, excluding the processes of field ionization, Coulomb explosion, and field-assisted dissociation. They found that dissociative ionization of methanol induced by ultrashort laser pulses has been studied at wavelengths of 400 nm and 800 nm with moderate intensity (10^{12}–10^{13} W/cm^2). The laser power dependence of ionic species shows that multi-photon ionization causes an excitation with a total energy from 11 to 15 eV. Comparing the current results with those of conventional VUV photodissociation experiments, they concluded that the molecules are excited to the X, A, B and C states of the ion, resulting in the CH_4O^+, CH_3O^+, CH_3^+ and CHO^+ ions, respectively.

However, the field-assisted stepwise dissociation mechanism of polyatomic molecules has been successfully applied to acetone (Tang et al., 2003), methane (Wang et al., 2003), acetaldehyde (Elshakre et al., 2003). Recently the stepwise dissociation of the symmetric triatomic CO_2 has been demonstrated (Elshakre, 2013) in the medium intensity of 10^{13}–10^{14} W/cm^2, by varying the electric field step-wisely resulting in a sequential bond breaking of the two bonds of CO_2. Therefore, the step-wise dissociation mechanism is challenged by investigating the dissociation of methanol, a molecule that is relatively more complex than CO_2, where methanol contains 6 atoms and constitutes three different types of bonds, making this case more complex than that of the symmetric triatomic CO_2. This study is marking a continuous effort to understand the step-wise dissociation mechanism of more complex molecules in this medium intensity range. Therefore, this study addresses the field ionization and field dissociation approaches demonstrating the dissociative ionization using a different approach from the MPI implemented by Ueda et al. (Hatamoto et al., 2007).

2. Experimental

The laser system used in this study is shown in Fig. 1, which is a home-built mode-locked femtosecond Ti:sapphire oscillator (The home-built oscillator and the laser facility used in this work is located at the Molecular Reaction Dynamics Laboratory, Institute of Chemistry, Chinese Academy of Science, Beijing, China) which was pumped by a diode-pumped, frequency-doubled laser (Verdi Coherent). As a seed pulse, the 800 nm 30 fs laser pulse generated by the oscillator was stretched and then led to a multipass Ti: Sapphire amplifier (Quantronix, Odin) which was pumped by the

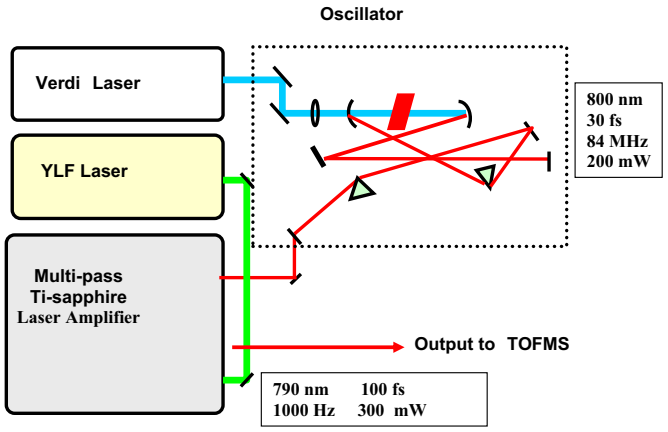

Fig. 1. Experimental lay out of the laser system coupled to the time-of-flight mass spectrometer (TOF-MS).

second harmonic of a Nd:YLF laser. The amplified fs laser pulse was compressed to 100 fs producing energy output of ~300 μJ per pulse. The amplified fs pulse was focused into the chamber of the linear TOF mass spectrometer by a 15 cm focal lens. The gaseous molecules were continuously effused into the chamber through an orifice with 500 μm, with a background pressure of 1.2×10^{-6} Torr and methanol gas pressure of 3.4×10^{-6} Torr. The calculated number density of methanol at this temperature was 1.1×10^{11} cm^{-3}, a value implying negligible mass/charge effect. However, the background pressure used in the measurements is relatively high implying a relatively high mass/charge effect which may result in mass peak broadening, particularly at high laser intensity due to overlap of neighboring mass peaks. The gas molecules were crossed against the focused laser beam, with a calculated Rayleigh range of 5.5 mm. The fragment ions produced in the laser were extracted using 900 V in a two-stage electric field and fly freely to a dual micro-channel plate (MCP) through a 50-cm free-field flight tube. The ion signal was detected using MCP and acquired using a 100 MHz high-speed transient recorder and then transferred to a computer for data acquisition. The mass spectra of the dissociative ionization results are shown in Fig. 2.

Laser intensity measurements are a critical part of the ionization studies. The intensity measurements are difficult because the high power densities would damage detectors if exposed to the focussed beam spot. Moreover, the intensity is dependent upon the spatial pulse profile and varies with the distance from the focal point. A reliable method of measuring the intensity at the focused laser spot is the measurements of the 'appearance intensity' (Chang et al., 1993) and 'saturation intensity' (Perry et al., 1988) of any well-studied ion, like Xe^+. The appearance intensity, I_{ap}, is the lowest laser intensity required for the detection of a minimum number of ions N_{ap}, which is determined by the overall detection efficiency of the ion extraction, mass filter and detector system. Using the closed-form solutions suggested by Chang et al. (Chang et al. 1993),

$$I_{ap}=\frac{\frac{2}{3}E_k^{3/2}}{\ln\left((6\omega_0E_k)\left(\frac{2\tau}{1.76}\right)\left(\frac{\rho\pi V_0}{Nop}\right)\right)}$$

where E_k is twice the ionization energy, ω_0 is the 1/e radius of the spot, τ is the temporal pulse width, $V_0=\pi^2\,\omega_0{}^4/\lambda$ with λ being the light wavelength. The theoretical appearance intensity for Xe^+ was calculated and equated to the intensity at the corresponding experimental energy.

Taking the Xe atomic beam density at the interaction region as 10^{11} cm^{-3} in the experiment, $N_{ap}=1$ as the minimum detectable number of Xe^+ ions, ω_0 is the 1/e radius (in microns) of the