



Research paper

Channel-specific photoelectron angular distribution in laboratory and molecular frames for dissociative ionization of methanol in intense ultraviolet laser fields



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ABSTRACT

We investigate dissociative ionization of CH₃OH in an intense laser field (398 nm, 76 fs, 8.9×10^{12} W/cm²) by photoelectron-photoion coincidence momentum imaging. It is revealed from the analysis of the channel-specific photoelectron angular distributions that CH₃OH is decomposed into CH₂OH⁺ + H after the four-photon ionization to the vibrationally highly excited states of the electronic ground state of CH₃OH⁺ and into CH₃⁺ + OH after the five-photon ionization to the second electronically excited state of CH₃OH⁺, and that these two channels are also opened after CH₃OH⁺, prepared by the four-photon ionization, is photoexcited further into the electronically excited states.

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1. Introduction

Molecules in intense laser fields undergo a variety of dynamical processes in which electron ejection and chemical bond breaking proceed simultaneously, such as dissociative ionization [1] and multiple ionization leading to Coulomb explosion [2,3]. In an early study of the multiphoton dissociative ionization of C₂H₄ induced by an intense laser field [4], it was shown that electronically excited states of parent cations, C₂H₄⁺, are prepared at the moment of photoelectron emission on the basis of the yields of the fragment ions as a function of the laser intensity. Since then, it has been an attractive research theme how such electronically excited parent ions are prepared by the irradiation of an ultrashort intense laser pulse and how the prepared electronically excited states decay by the fragmentation [5–12]. By using the method called photoelectron-photoion coincidence momentum imaging (PEPICO-MI), we investigated dissociative ionization of ethanol (C₂H₅OH) in intense near-infrared and ultraviolet (UV) laser fields [6,7,11], and revealed that C₂H₅OH⁺ is prepared by two different routes, that is, an immediate creation of the electronically excited state associated with photoelectron emission and a stepwise creation by photoexcitation of the electronic ground C₂H₅OH⁺ to the electronically excited state, on the basis of the analysis of the channel-specific photoelectron spectra and the energy correlation between photoelectrons and fragment ions.

It is true that the PEPICO-MI method is a powerful technique for revealing the dissociative ionization pathways, but only the correlations between the kinetic energies of photoelectrons and photoions are sometimes inadequate to discriminate different routes through which electronically excited cations are prepared, especially when more than one electronic state is created simultaneously. Because the photoelectron angular distribution (PAD) [13,14] reflects sensitively the electronic states of cations created upon the ionization, the dissociative ionization pathways can be clarified more if the PADs are constructed by the results of the PEPICO-MI measurements.

In the present study, in order to reveal the mechanisms of the creation of electronically excited parent ions in the dissociative ionization of CH₃OH in an ultrashort intense UV laser pulse, we performed the PEPICO-MI measurements, and constructed channel-specific laboratory-frame (LF) PADs and channel-specific molecular-frame (MF) PADs. From the LF-PADs and MF-PADs for the formation of the parent ions CH₃OH⁺ and for the two dissociation pathways, CH₃OH⁺ → CH₂OH⁺ + H and CH₃OH⁺ → CH₃⁺ + OH, we reveal how the different electronic states are created by multiphoton ionization and how these electronic states decay through the specific fragmentation channels.

2. Experimental setup

The detail of the photoelectron-photoion coincidence momentum imaging apparatus was previously reported [11,15]. Briefly,

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linearly-polarized near-infrared laser pulses were generated by a Ti:Sapphire regenerative amplifier. By second-harmonic generation of the near-infrared pulses using a β -barium borate crystal (0.2 mm thick, type I), UV pulses (0.1 mJ, 398 nm, 76 fs, 1 kHz) were obtained. In a separate experiment with the same laser condition, a photoelectron spectrum of Kr was recorded. It was found that the ponderomotive shift [16] of a pair of peaks assigned to five-photon ionization to $^2P_{3/2}$ and $^2P_{1/2}$ of Kr^+ was 0.13 eV, from which the laser field intensity at the focal point was estimated to be $8.9 \times 10^{12} \text{ W/cm}^2$.

A photoelectron and a photoion created simultaneously at the crossing point of the laser beam and the effusive molecular beam of pure methanol vapor were accelerated to the opposite directions and focused respectively on the two position sensitive detectors placed at the opposite sides of the vacuum chamber. Electrostatic lenses were equipped so that the three-dimensional (3D) momentum focusing conditions [15,17] are fulfilled. The 3D momentum vectors of the photoelectron and the photoion detected in coincidence were obtained from their arrival times and positions on the respective detectors. In order to secure the coincidence conditions, the detection event rate was kept around 0.3 events per laser pulse by controlling the flow of methanol vapor using a variable leak valve.

3. Results and discussion

3.1. Photoelectron spectra

Fig. 1 shows the kinetic energy spectra of the photoelectrons detected in coincidence with (a) CH_3OH^+ , (b) CH_2OH^+ , and (c) CH_3^+ . The photoelectron kinetic energy, E_{elec} , was obtained directly from the recorded 3D momentum vector of each detected photoelectron. In the photoelectron spectrum associated with the formation of the parent ion, hereafter called the CH_3OH^+ channel (Fig. 1a), a strong peak is seen at $E_{\text{elec}} = 1.2 \text{ eV}$. In addition, one weak peak can be seen at 4.3 eV. As shown in Fig. 2 [18–21], if CH_3OH^+ is prepared in the \tilde{X} state after four-photon absorption,

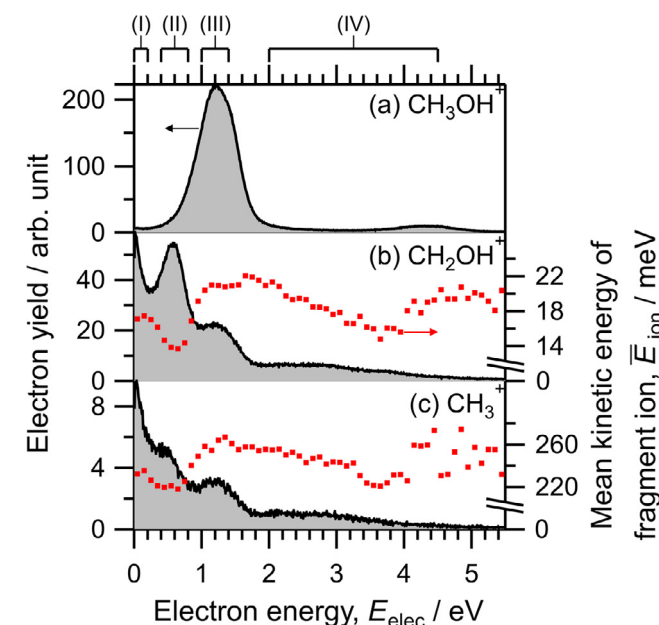


Fig. 1. Photoelectron energy spectra (solid line) recorded in coincidence with the formation of (a) CH_3OH^+ , (b) CH_2OH^+ and (c) CH_3^+ . The mean kinetic energies of the fragment ions, (b) CH_2OH^+ and (c) CH_3^+ , are plotted with red dots as a function of photoelectron energy. See the text for details of the energy ranges (I)–(IV).

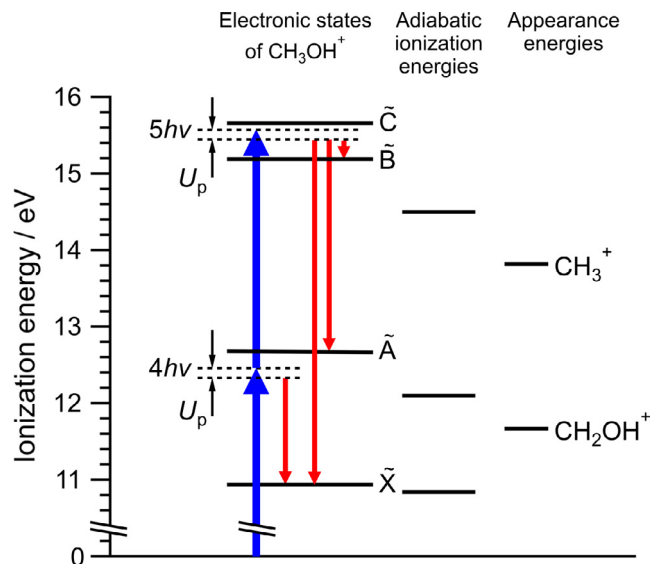


Fig. 2. Energy diagram of CH_3OH^+ based on the photoelectron spectrum recorded previously by a He (I) light source [18]. The vertical ionization energies [18] to the respective electronic states of \tilde{X} (10.94 eV), \tilde{A} (12.68 eV), \tilde{B} (15.19 eV), and \tilde{C} (15.66 eV) states of CH_3OH^+ measured from the electronic ground state of CH_3OH are shown by the horizontal bars on the left side. The three horizontal bars in the center represent the adiabatic ionization energies of the \tilde{X} , \tilde{A} and \tilde{B} states [19], which are lower than the respective vertical ionization energies by 0.1, 0.6 and 0.7 eV, respectively. The ponderomotive energy U_p at the laser intensity of $8.9 \times 10^{12} \text{ W/cm}^2$ is $U_p = 0.13 \text{ eV}$. The length of the vertical red arrows represents the kinetic energy of photoelectrons. The appearance energies for the dissociation channels producing CH_2OH^+ (11.67 eV) [20] and CH_3^+ (13.82 eV) [21] are also shown. The thermochemical threshold (13.76 eV) [22] of the CH_3^+ channel adopted in Section 3.4 is consistent with the appearance energy (13.82 eV) [21].

the excess energy above the vertical ionization potential $I_p(\tilde{X}) = 10.94 \text{ eV}$ [18] is calculated to be 1.39 eV by taking account of the ponderomotive energy shift. This excess energy, which is close to the peak energy of the strong peak in Fig. 1a, indicates that the \tilde{X} state of CH_3OH^+ is created through four-photon ionization of CH_3OH . The weak peak at $E_{\text{elec}} = 4.3 \text{ eV}$ can be assigned to five-photon above-threshold-ionization (ATI) to the \tilde{X} state of CH_3OH^+ , because the energy separation between this weak peak and the strong peak at $E_{\text{elec}} = 1.2 \text{ eV}$ is in good agreement with one-photon energy of 3.1 eV.

In the photoelectron spectrum associated with the formation of CH_2OH^+ (Fig. 1b), there are three peaks in the energy ranges of (I) $\sim 0 \text{ eV}$, (II) $\sim 0.6 \text{ eV}$ and (III) $\sim 1.2 \text{ eV}$, and a weak and broad feature can be seen in the energy range (IV) between 2.0 and 4.5 eV. The fragment ion, CH_2OH^+ , is produced from the dissociation pathway of



We call hereafter this pathway (1) the CH_2OH^+ channel.

The photoelectron spectrum associated with the formation of CH_3^+ (Fig. 1c) is found to be similar to Fig. 1b. Two peaks can be seen in the energy ranges of (I) $\sim 0 \text{ eV}$ and (III) $\sim 1.2 \text{ eV}$, and a weak and broad feature can also be seen in the energy range (IV) between 2.0 and 4.5 eV. In the energy range (II), only a shoulder can be seen. The fragment cation, CH_3^+ , is produced from the dissociation pathway of



We call hereafter this pathway (2) the CH_3^+ channel.

For the CH_2OH^+ channel, judging only from the kinetic energy of the photoelectrons, the peak in the energy range (II) can be interpreted by two possible ionization pathways: (i) four-photon

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