

Correlation between photoelectron emission and fragment recoil of methanol in intense laser fields

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Abstract: Dissociative ionization of methanol in an intense laser field is investigated using photoelectron-photoion coincidence momentum imaging. Energy and angular correlations between a photoelectron and a fragment ion reveal the ionization and subsequent electronic excitation processes.

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1. Introduction

Ionization is a fundamental process for molecules in intense laser fields to trigger a variety of phenomena such as Coulomb explosion and high-order harmonic generation. It has been realized in these years that photoelectron emission proceeds not only from HOMO but also from inner valence orbitals [1,2]. In the dissociative ionization of molecules in an intense laser field, electronic excitation plays an essential role in governing the subsequent fragmentation dynamics. Recent advances in photoelectron-photoion coincidence momentum imaging techniques have revealed the existence of the electronic excitation processes occurring after the ionization and leading to the dissociation. For ethanol, C₂H₅OH, based on the energy correlation between a photoelectron and a fragment ion as well as on the channel-specific photoelectron spectra, we were able to identify securely two different routes through which the electronic excitation leading to the dissociation is achieved; (i) direct preparation of the electronically excited states at the moment of photoelectron emission and (ii) electronic excitation after the electronic ground state is formed upon the photoionization [3]. In the present study, we investigate dissociative ionization of methanol, CH₃OH, in an intense laser field, and reveal the angular correlation between the photoelectron emission and the fragment recoil as well as their kinetic energy correlation.

2. Experiment

Linearly polarized femtosecond ultraviolet (UV) pulses (70 fs, 398 nm, 1 kHz) were obtained by frequency-doubling of near-infrared laser pulses (50 fs, 791 nm) generated by a Ti:sapphire regenerative amplifier. The UV laser pulses were focused on an effusive beam of a neat methanol vapor. The laser peak intensities at the focal spot were estimated to be 1×10^{13} W/cm². A photoelectron and a photoion generated from the same methanol molecule were extracted to the opposite directions, and were focused on two position sensitive detectors by electrostatic lenses. From their arrival times and positions on the detectors, the three-dimensional momentum vectors for the photoelectrons and the ions were obtained.

3. Results and discussion

Photoelectron energy spectra detected in coincidence with CH₃OH⁺, CH₂OH⁺, and CH₃⁺ are shown in Fig. 1. It has been known that CH₃OH⁺ can survive only in the lower vibrational levels of the electronic ground state than the threshold energy for the H elimination, and that dissociation takes place when CH₃OH⁺ is electronically excited. Therefore, the peak appearing at the electron kinetic energy of $\varepsilon \sim 1.2$ eV in the photoelectron spectra correlated with the CH₃OH⁺ formation is assigned to the four-photon ionization to the electronic ground state. For the fragment channels, the channel-specific photoelectron spectra exhibit different features from that for the CH₃OH⁺ formation, suggesting that different electronic and vibrational state distributions of CH₃OH⁺ are prepared at the moment of photoelectron emission for the respective product channels.

For the fragment channels to form CH₂OH⁺ and CH₃⁺, the peaks in the photoelectron spectrum appears at $\varepsilon \sim 0$ and 0.6 eV in addition to $\varepsilon \sim 1.2$ eV. The peak at $\varepsilon \sim 0$ eV is assigned to the four-photon ionization to the first electronically excited state and/or to the five-photon ionization to the second electronically excited state. The peak at $\varepsilon \sim 0.6$ eV is assigned to the four-photon ionization to the vibrationally excited states in the electronic ground state and/or to the five-photon ionization to the second electronically excited state. The broad features at $\varepsilon \sim 1.2$ eV for these fragmentation channels suggest the presence of the electronic excitation subsequent to the ionization to the ground state. The mean kinetic energy release (KER) of the fragment ions is also plotted in Fig. 1 as a function of ε .

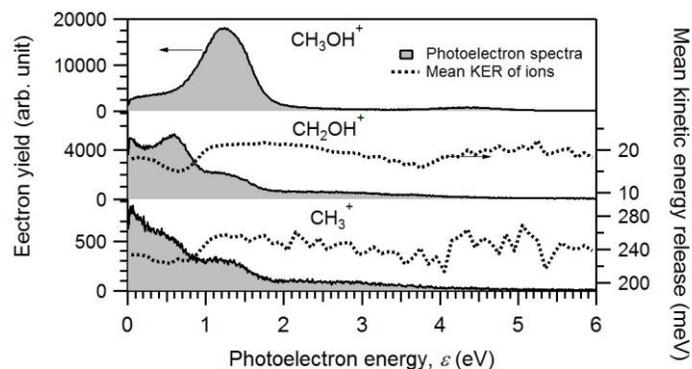


Fig. 1. Channel-specific photoelectron spectra (solid line with shaded area) for CH_3OH^+ , CH_2OH^+ and CH_3^+ (from top), and the mean kinetic energy release (dotted line) of fragment ions specified by the photoelectron energy.

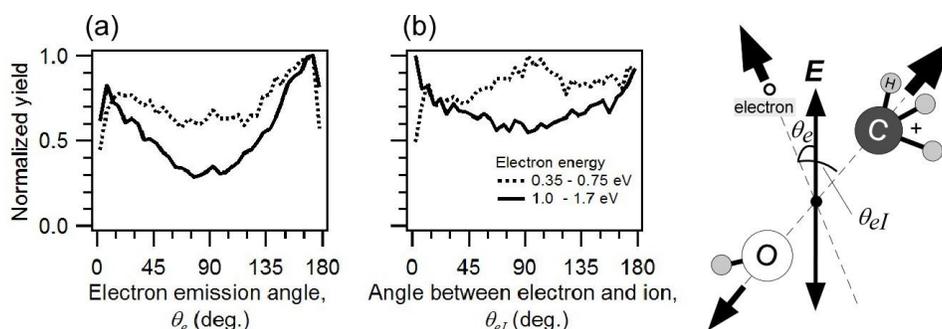


Fig. 2. Angular distributions of photoelectron emission correlated with the CH_3^+ formation with respect to (a) the laser polarization direction and (b) the recoil direction of CH_3^+ . The respective distributions are plotted for the events with the photoelectron energy in the ranges of 0.35-0.75 (solid line) and 1.0-1.7 eV (dotted line). The angles among the directions of the laser polarization, electron emission, and CH_3^+ recoil are illustrated on the right side.

The variation in the KER indicates that the internal energy gained from the laser field depends on the electronic and vibrational states prepared at the moment of photoelectron emission. The larger KER at $\epsilon \sim 1.2$ eV suggests the higher-lying electronic states are prepared by the subsequent excitation after the photoelectron emission.

In addition to the energy correlation, the direction of the photoelectron emission provides another insight into the ionization dynamics. As shown in Fig. 2(a) for the CH_3^+ formation, the photoelectron angular distribution (PAD) with respect to the laser polarization direction at $\epsilon \sim 0.6$ eV (0.35-0.75 eV) exhibits a more isotropic distribution than the PAD at $\epsilon \sim 1.2$ eV (1.0-1.7 eV), suggesting that a photoelectron is emitted from different molecular orbitals upon the photoionization. Indeed, the ionization to the second electronically excited state plays an important role at $\epsilon \sim 0.6$ eV for the CH_3^+ formation. The PADs with respect to the direction of the CH_3^+ recoil at $\epsilon \sim 0.6$ and 1.2 eV exhibit more striking difference as shown in Fig. 2(b). The molecular-frame PAD at $\epsilon \sim 0.6$ eV shows a peak at 90° , but that at $\epsilon \sim 1.2$ eV shows a node at 90° . This marked contrast is the evidence that a photoelectron is ejected from the two different orbitals resulting in these two different photoelectron energies. It should be emphasized that this contrast can only be extracted when both a photoelectron and a photoion are detected in coincidence.

References

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