

Deformation of a Molecular Orbital in Ethanol Induced by an Intense Laser Field

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In laser fields with intensities as high as 10^{14} W/cm², molecules are ionized through electron tunneling. It is understood that the tunnel ionization depends on the spatial density distribution and binding energy of the molecular orbital (MO) from which an electron is ejected. This is based on the angular dependence of the ionization probability measured for diatomic or triatomic molecules [1–5]. Recently, it has been suggested that MOs in molecules larger than the triatomic ones are deformed by laser electric fields [6,7]. As the molecular size increases, the energy spacing between MOs decreases, leading to strong interactions among MOs in laser electric fields.

In the present study, we derive the molecular frame photoelectron angular distribution (MFPAD) of the dissociative ionization of ethanol ($\text{CH}_3\text{CD}_2\text{OH}$) in an intense near-infrared laser field ($I_0 \approx 8 \times 10^{13}$ W/cm², $\lambda \approx 800$ nm). The energy levels from HOMO-1 to HOMO-4 are close in a small energy range of 3 eV. Additionally, photoelectron-photoion coincidence measurement with He(I) at 21.2 eV showed that electron ejection from different MOs results in different fragment ions [8]. Therefore, identifying the fragment ion allows us to identify the MO from which the electron was ejected.

In our experiment, we use a partially deuterated $\text{CH}_3\text{CD}_2\text{OH}$ sample to avoid producing different fragment ions with the same mass. The vaporized sample is introduced in an ultrahigh-vacuum chamber through a micro-syringe [9], and the molecular effusive beam is irradiated with a circularly polarized laser pulse, which singly ionizes an unaligned molecule. A linearly polarized femtosecond laser pulse from Ti:Sapphire regenerative and multi-pass amplifiers ($\Delta\tau \approx 60$ fs, 1 kHz) is converted into a circularly polarized pulse by passing through a quarter-wave plate. The photoelectron drifts perpendicular to the laser electric field at the moment of ionization [3,4]. The recoil direction of a fragment ion reflects the orientation of the parent molecule. We detect an electron and a fragment ion in coincidence with two position-sensitive detectors to determine the angle between their recoil vectors. MFPADs are derived by taking account of the electron drift.

Figures 1A and B show the MFPADs of the CD_2OH^+ and CH_3CD_2^+ production channels, respectively. The CD_2OH^+ channel shows preferential electron ejection from the CH_3 side of $\text{CH}_3\text{CD}_2\text{OH}$ (Fig. 1A), whereas the MFPAD of the CH_3CD_2^+ production channel is almost isotropic (Fig. 1B). A previous measurement using He(I) suggested that (i) CD_2OH^+ is produced from the first electronically excited state of the parent

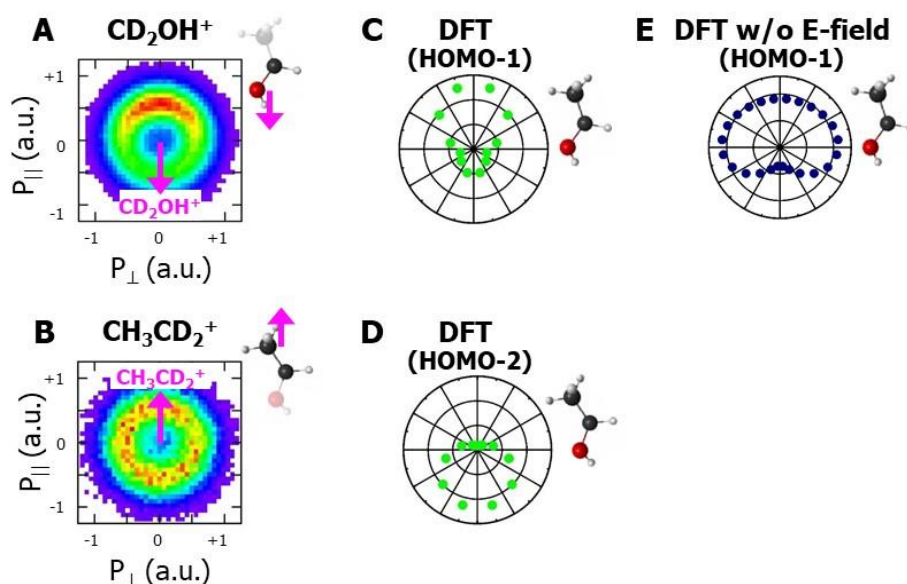


Fig. 1. (A and B) Electron momentum distribution in the molecular frame for the CD_2OH^+ and the CH_3CD_2^+ channels, respectively. (C and D) Simulated MFPADs of HOMO-1 and HOMO-2 in a static electric field. (E) Simulated MFPAD of HOMO-1 without the influence of the electric field. The simulated results are convoluted with the experimental angular uncertainty ($\pm 45^\circ$).

CH₃CD₂OH⁺ ion and (ii) CH₃CD₂⁺ is produced from the second excited state of CH₃CD₂OH⁺ [8]. Therefore, the MFPADs of the CD₂OH⁺ and CH₃CD₂⁺ channels correspond to the electron ejection from HOMO-1 and HOMO-2, respectively.

We simulate the angular dependence of the tunnel ionization rate and compare it with the experimental results. We use density functional theory (DFT) with the KLI-SIC potential, which reproduces the HOMO binding energy. We solve the complex eigen-energy of the Kohn–Sham Hamiltonian under a static electric field and absorbing potential far outside the molecule. The tunnel ionization rate is obtained from the imaginary part of the Gamow state eigenvalue [10]. Figures 1C and D show the simulated MFPADs for HOMO-1 and HOMO-2, respectively. The simulated HOMO-1 MFPAD (Fig. 1C) shows preferential electron tunneling in the direction along the CH₃ recoil and agrees reasonably with the measured one for the CD₂OH⁺ channel (Fig. 1A). Our simulations do not reproduce the measured HOMO-1 MFPAD unless we account for MO deformation in the electric field. Figure 1E shows the MFPAD for the field-free HOMO-1 from which the MO deformation is excluded. The MFPAD for the field-free HOMO-1 shows preferential tunneling in the lateral direction with respect to the CD₂OH⁺ recoil direction (Fig. 1E). This discrepancy suggests that HOMO-1 deformation is needed to explain the preferential electron ejection from the CH₃ side derived in the measured MFPAD of the CD₂OH⁺ channel.

For HOMO-2, the simulation indicates that the electron is ejected preferentially from the OH side (Fig. 1D). However, the measured MFPAD for the CH₃CD₂⁺ channel is almost isotropic (Fig. 1B). In the intense laser field, the second electronically excited state of CH₃CD₂OH⁺ can be produced by not only electron ejection from HOMO-2 but also from HOMO or HOMO-1 followed by the electronic excitation of CH₃CD₂OH⁺ to the second electronically excited state [9]. The isotropic MFPAD suggests that the stepwise channels contribute comparatively to the ionization to form the second excited state of CH₃CD₂OH⁺, which has a hole in HOMO-2.

In summary, we measure MFPADs of dissociative ionization channels of ethanol CH₃CD₂OH in a circularly polarized laser field with an intensity of $I_0 \approx 8 \times 10^{13}$ W/cm². The MFPAD of the CD₂OH⁺ channel shows reasonable agreement with the simulated MFPAD for HOMO-1. Our DFT simulations reveal that HOMO-1 is deformed appreciably by the laser electric field. The measured isotropic MFPAD of the CH₃CD₂⁺ channel cannot be reproduced by the simulated MFPAD for HOMO-2, suggesting that the electronic excitation following the electron ejection from HOMO and HOMO-1 takes place significantly.

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