Real-time probing of ultrafast hydrogen migration in methanol in intense femtosecond laser fields

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[Abstract] Ultrafast dynamics of methanol in intense laser field was investigated by pump-probe experiments using 40 fs pump pulses (800 nm, 63 TW/cm²) and 6 fs probe pulses (780 nm, 420 TW/cm²). It was found that the yields of the fragment ions generated from the Coulomb explosion of CH₃OH⁺ increase as the delay time between the pump and probe pulses increases within the pump pulse duration. We attributed this increase of the ion yields to the mixing of electronically excited configurations of CH₃OH⁺ by the pump laser field. In addition, by the comparison of CH₃⁺ + OH⁺ and CH₂⁺ + OH₂⁺ dissociation channels, we found that the ultrafast hydrogen migration proceeds within 7 fs.

[Introduction] It has been known that hydrogen atom migration proceeds within a hydrocarbon molecule after it is irradiated with a femtosecond laser pulse. It has been revealed [1] that there are two types of hydrogen migration processes in methanol cation, CH₃OH⁺; (i) ultrafast hydrogen migration occurring within the period of the pump pulse duration and (ii) slower hydrogen migration occurring after the irradiation of the pump pulse. Recently, by performing the pump-probe experiment using ~6 fs few-cycle pulses, we identified that the ultrafast hydrogen migration in CH₃OH⁺ is completed within ~25 fs [2]. However, it has been still unclear how fast the hydrogen migration could proceed in CH₃OH⁺ when it is being exposed to intense laser fields.

In the present study, we investigate ultrafast dynamics of CH₃OH⁺ occurring within the laser field by pump-probe measurements using a pump pulse with the pulse width of ~40 fs and a probe pulse with the pulse width of ~6 fs. Figure 1 shows the schematic image of the pump-probe scheme in which CH₃OH is ionized to CH₃OH⁺ by the pump laser pulse and CH₃OH⁺ is irradiated with the probe pulse during the time when CH₃OH⁺ is still being irradiated with the pump laser pulse.

[Methods] Linearly polarized laser pulses generated by a Ti:sapphire laser system (800 nm, 5 kHz, 0.4 mJ, ~30 fs) were split into two by a polarizer and a half-wave plate. One of the split laser pulses were compressed by an Ar-filled hollow-core fiber and a set of chirped mirrors. The generated few-cycle probe laser pulses (~6 fs) and the other split laser pulses (~40 fs) were overlapped with each other coaxially and were focused on an effusive molecular beam of
methanol in a vacuum chamber. The peak laser-field intensities at the focal point was estimated to be $6.3 \times 10^{13}$ W/cm$^2$ for the pump pulse and $4.2 \times 10^{14}$ W/cm$^2$ for the probe pulse. Fragment ions generated by the laser pulses were accelerated and were focused on a position sensitive detector by electrostatic lenses. The three-dimensional momentum vectors of the fragment ions were determined from their detected positions and flight times at the detector. Fragment ions generated from Coulomb explosion of CH$_3$OH$^{2+}$ were extracted by applying the momentum conservation conditions.

**Results and discussion** The yields of the five dissociation channels are shown in Fig. 2 as a function of the pump-probe delay time $\Delta t$. In the region A ($\Delta t < -20$ fs), the yields of H$^+$ and CH$_3^+$ increase as $\Delta t$ decreases, which can be attributed to the enhanced ionization associated with the elongation of the C-H and C-O nuclear distances, respectively. In the region C ($\Delta t > 20$ fs), small peak profiles can be seen at $\Delta t \sim 60$ fs and $\Delta t \sim 90$ fs in all the five channels. These peaks can be interpreted as a periodical increase of the yields associated with the C-O stretching vibration of CH$_3$OH$^+$. In the region B ($-20$ fs $< \Delta t < 20$ fs) where the pump and the probe pulses overlap, the yields of the four channels increase as $\Delta t$ increases. In this region, CH$_3$OH$^+$ generated by the pump pulse are continuously exposed to the pump laser field until it is ionized into CH$_3$OH$^{2+}$ by the probe pulse. Therefore, these increases indicate that the extent of the mixing of the electronically excited configurations into the electronic ground CH$_3$OH$^+$ becomes larger in the course of the interaction with the intense laser field, resulting in the larger ionization probability of CH$_3$OH$^+$.

Figure 3 shows the yields of the CH$_3^+$ + OH$^+$ dissociation channel (non-migration channel) and CH$_2^+$ + OH$_2^+$ dissociation channel (migration channel). A distinct difference was found in $\Delta t < 0$ fs region, where CH$_3$OH is ionized first by the 6 fs pulse and the resultant CH$_3$OH$^+$ is ionized into CH$_3$OH$^{2+}$ by 40 fs pulse. As $\Delta t$ decreases, the yield of the non-migration channel starts increasing at $\Delta t \sim -20$ fs while the yield of the migration channel starts increasing at $\Delta t = -7$ fs, indicating that the ultrafast hydrogen migration starts proceeding within 7 fs in the intense laser field.

**References**
