4P015

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/cm^2) and 6 fs probe pulses (780 nm, 420 TW/cm^2). It was found that the yields of the fragment ions generated from the Coulomb explosion of CH_3OH^{2+} 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 CH_3OH^+ by the pump laser field. In addition, by the comparison of $CH_3^+ + OH^+$ and $CH_2^+ + OH_2^+$ 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, CH_3OH^+; (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 CH_3OH^+ is completed within ~25 fs [2]. However, it has been still unclear how fast the hydrogen migration could proceed in CH_3OH^+ when it is being exposed to intense laser fields.

In the present study, we investigate ultrafast dynamics of CH_3OH^+ 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 CH_3OH is ionized to CH_3OH^+ by the pump laser pulse and CH_3OH^+ is irradiated with the probe pulse during the time when CH_3OH^+ is still being irradiated with the pump laser pulse.

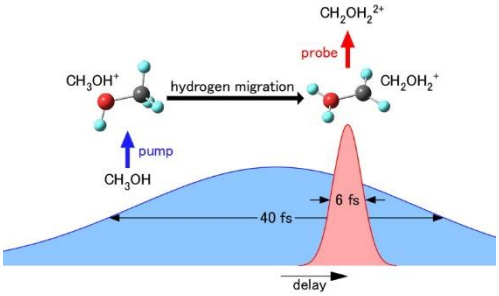

Fig. 1. Schematic image of the experiment.

[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 6.3×10^{13} W/cm^2 for the pump pulse and 4.2×10^{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_3OH^{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 Δt. In the region A ($\Delta t < -20$ fs), the yields of H^+ and CH_3^+ increase as Δt 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_3OH^+. 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 Δt increases. In this region, CH_3OH^+ generated by the pump pulse are continuously exposed to the pump laser field until it is ionized into CH_3OH^{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_3OH^+ becomes larger in the course of the interaction with the intense laser field, resulting in the larger ionization probability of CH_3OH^+.

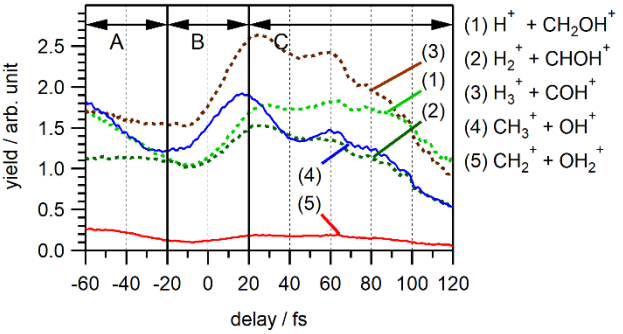

Fig. 2. The yields of the five different Coulomb explosion channels of methanol dication, CH_3OH^{2+}.

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_3OH is ionized first by the 6 fs pulse and the resultant CH_3OH^+ is ionized into CH_3OH^{2+} by 40 fs pulse. As Δt 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.

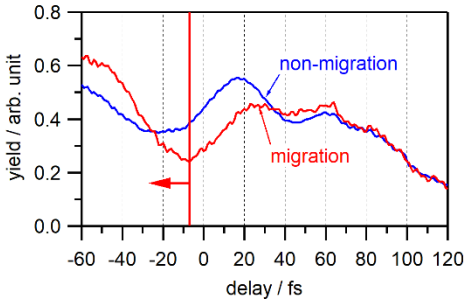

Fig. 3. The scaled yields of the non-migration ($CH_3^+ + OH^+$) channel and migration channel ($CH_2^+ + OH_2^+$) channel scaled by the corresponding yields obtained when only the 6 fs pulses were used.

[References]

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