Communication: Two stages of ultrafast hydrogen migration in methanol driven by intense laser fields

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Hydrogen migration in methanol induced by an intense laser field (0.2 PW/cm²) is investigated in real time by a pump-probe coincidence momentum imaging method. The observed temporal evolution of the kinetic energy spectra reveals that there are two distinctively different stages in the hydrogen migration processes in the singly charged methanol: ultrafast hydrogen migration occurring within the intense laser field (∼38 fs) and slower postlaser pulse hydrogen migration (∼150 fs). © 2010 American Institute of Physics. [doi:10.1063/1.3473931]

When molecules are exposed to an intense laser field, they exhibit a variety of characteristic dynamics, such as ionization, isomerization, and fragmentation. In particular, a so-called hydrogen migration process within a hydrocarbon molecule, accompanying the chemical-bond rearrangement associated with ultrafast motion of hydrogen atom(s) or proton(s) induced by an intense laser field, has become one of the most attractive research themes in these years. The proton motion within a molecule was considered to proceed very rapidly, and it was predicted that this process could occur within the light field. This argument was based on the assumption that those doubly or triply charged species formed by the most intense part of the laser pulse and that undergo Coulomb explosion immediately after they are formed by the most intense part of the laser pulse and that the hydrogen migration should proceed before the Coulomb explosion. The observation that the extent of anisotropy in the ejection direction of the fragment ions for the migration pathways is the same as that for the nonmigration pathways was considered to be an evidence that ultrafast hydrogen migration proceeds within the laser field. The other evidence for the probability of hydrogen migration occurring within the laser pulse was suggested from the polarization dependence of the kinetic energy distribution of H₂⁺ appearing in the TOF spectra of linear alcohols. On the other hand, a postpulse slower motion of an deuterium atom was shown for deuterated acetylene dication.

In view of the importance of the hydrogen migration in controlling chemical bond breaking and formation processes, it is necessary to exploit experimentally how the large-scale proton migration induced by an intense laser field indeed proceeds along the skeletal bond(s) such as C–C, C–O, and C–N bonds within a molecule. However, no experiments have been reported so far to distinguish the hydrogen (or a proton) migration within the laser field from the postlaser-pulse hydrogen migration, and tracing the ultrafast hydrogen migration in real time is indeed one of the most attractive challenges in ultrafast molecular science.

In the present paper, we probe the hydrogen migration dynamics in methanol in real time, and discover that there are two stages in the ultrafast hydrogen migration processes, that is, the instantaneous transfer of a proton from the carbon atom site to the oxygen atom site occurring within the ultrashort laser pulse, and the unimolecular isomerization processes occurring with a time scale of ∼150 fs after the light-matter interaction.

The method we employed is the pump-probe coincidence momentum imaging (CMI), and two types of two-body Coulomb explosion processes are probed in real time as a function of the time delay, Δt, between the pump and probe pulses, that is, the pathway in which the C–O bond is broken without the hydrogen migration:

\[
\text{CH}_3\text{OH}^2+ \rightarrow (\text{CH}_3\cdots\text{OH})^{2+} \rightarrow \text{CH}_3^+ + \text{OH}^+. \quad (1)
\]

and the pathway in which the C–O bond is broken after the migration of one hydrogen atom from the methyl group to the hydroxyl group:

\[
\text{CH}_3\text{OH}^2+ \rightarrow (\text{CH}_3\cdots\text{OH})^{2+} \rightarrow \text{CH}_2^+ + \text{OH}_2^+. \quad (2)
\]

The experiment was carried out by using a Ti:sapphire femtosecond laser system, which generates the laser pulses (5 kHz) with the central wavelength of ∼805 nm and the pulse duration of ∼38 fs measured by a SPIDER. A pair of linearly polarized laser pulses with the same pulse energies (40 μJ/pulse) was generated through a Michelson-type interferometer with a variable time delay Δt (=100–800 fs). The two laser pulses were then focused onto an effusive molecular beam of methanol (CH₃OH) in an ultrahigh vacuum chamber with a base pressure of ∼3×10⁻¹¹ Torr. The intensity at the focal spot was ∼2×10¹⁴ W/cm² for

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both pump and probe pulses. The minimum time delay of $\Delta t=100$ fs was chosen to avoid the optical interference of the two laser pulses. The increment of the time delay was set to be 50 fs with the uncertainty of 0.5 fs. For the CMI measurements of the fragment ions, the detailed descriptions can be found in Ref. 16.

From the observed CMI maps of $\text{CH}_3^+$ and $\text{CH}_2^+$ appearing in coincidence respectively with $\text{OH}^+$ and $\text{OH}_2^+$, as $\Delta t$ increases, a new circular momentum component starts to emerge and its peak momentum value decreases gradually, showing that the dissociating singly charged molecular ions, ($\text{CH}_3\cdots\text{OH})^+$ and ($\text{CH}_2\cdots\text{OH}_2)^+$, prepared by the pump pulse are ionized further by the doubly charged molecular ions, $\text{CH}_2^+\cdots\text{OH}^+$ and $\text{CH}_2^+\cdots\text{OH}_2^+$, leading to the Coulomb explosion into $\text{CH}_3^+\pm\text{OH}^+$ and $\text{CH}_2^+\pm\text{OH}_2^+$, respectively.

Based on the three-dimensional momentum distributions of the fragment ions, the sum of the kinetic energy released from a pair of the fragment ions, $E_{\text{kin}}$, is obtained. The yield distributions of the two pathways, Eqs. (1) and (2), are plotted as functions of $\Delta t$ and $E_{\text{kin}}$ in two-dimensional (2D) contour patterns, as shown in Fig. 1. It can be seen in both cases that the 2D distributions can be categorized into two parts: the upper strip, where the kinetic energy distributions are independent of $\Delta t$, and the lower strip, where the peak position of the kinetic energy distributions shift toward lower energies as $\Delta t$ increases, exhibiting a time-dependent behavior.

The time-dependent lower strips in Figs. 1(a) and 1(b) are considered to reflect the temporal evolution of a dissociating wave packet of ($\text{CH}_3\cdots\text{OH})^+$ and that of ($\text{CH}_2\cdots\text{OH}_2)^+$, respectively. This means that ($\text{CH}_3\cdots\text{OH})^+$ and hydrogen-migrated ($\text{CH}_2\cdots\text{OH}_2)^+$ prepared by the pump laser pulse in the energy region higher than the dissociation barrier start the dissociation process, and after a certain temporal delay before the complete dissociation, the probe laser pulses ionize ($\text{CH}_3\cdots\text{OH})^+$ into ($\text{CH}_2\cdots\text{OH})^{2+}$, and ($\text{CH}_2\cdots\text{OH}_2)^+$ into ($\text{CH}_2\cdots\text{OH}_2)^{2+}$, projecting the respective wave packets of the singly charged dissociating ions onto the mostly repulsive Coulomb potential energy surfaces (PESs) of the doubly charged manifold. Therefore, from the kinetic energies released from the two-body Coulomb explosion processes through the nonmigration pathway, Eq. (1), and the migration pathway, Eq. (2), the distance between $\text{CH}_3^+$ and $\text{OH}^+$, and that between $\text{CH}_2^+$ and $\text{OH}_2^+$ can be estimated as a function of the delay time, that is, the evolution of the nuclear motions of ($\text{CH}_3\cdots\text{OH})^+$ and ($\text{CH}_2\cdots\text{OH}_2)^+$ ions can be plotted through the Coulomb explosion imaging.

It is commonly seen in Figs. 1(a) and 1(b) that the kinetic energy spread of the lower strip becomes narrower as $\Delta t$ increases, reflecting the shallower slopes of the dissociative PESs of the singly charged stage in the longer distance between the two fragment moieties. Assuming that the C–O bond breaking of the doubly charged species proceeds on the Coulombic repulsive PES, the released kinetic energy, $E_{\text{kin}}$, is converted into the distance between the charge centers of the two fragment moieties, $R$, by $E_{\text{kin}}=q_1q_2/(4\pi\epsilon_0R)$, where $q_1$ and $q_2$ are the charges of the two fragment ions. It is found that the distance, $R$, between the charge centers of $\text{CH}_3^+$ and $\text{OH}^+$ increases from 2.4 to 12.0 Å, and that between the charge centers of $\text{CH}_2^+$ and $\text{OH}_2^+$ increases from 2.8 to 12.0 Å when $\Delta t$ increases from 100 to 800 fs.

It can be seen that the time-independent upper strip in Fig. 1(a) is centered at $\sim 5.9$ eV, while the one in Fig. 1(b) is centered at $\sim 5.2$ eV. Contrary, when the nonmigration pathway through Eq. (1) and the migration pathway through Eq. (2) are induced only by the pump laser, the kinetic energy distributions of the fragment ions ejected from both the nonmigration and migration pathways are found to be peaked at $\sim 5.9$ eV. This interesting observation that the peak position of 5.2 eV for the migration pathway shown in Fig. 1(b) is lower by as much as 0.7 eV than the pump-only value of 5.9 eV can be interpreted in terms of the landscape of the PES of singly charged $\text{CH}_3^+$.

In Fig. 2, the calculated PESs of the ground states of $\text{CH}_3^+$ and $\text{CH}_2$ obtained by the density functional theory at the UB3LYP/6-31G(d) level with the GAUSSIAN 03
program\textsuperscript{17} are shown. It can be clearly seen that there are two minima at around A (1.37 Å, 45°) and B (1.46 Å, 145°) on the PES of CH\textsubscript{3}OH\textsuperscript{+}, representing the two geometrical structures, CH\textsubscript{2}OH\textsuperscript{+} and CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+}, respectively.

The difference in the kinetic energy distributions shown in the upper strips for CH\textsubscript{3}OH\textsuperscript{+} and CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+} can be ascribed to the difference in their geometrical structures. When the pump laser pulse prepares a molecular wave packet of CH\textsubscript{3}OH\textsuperscript{+} and that of CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+} on the PES around A and B shown in Fig. 2, the probe laser pulse, after a certain temporal delay, ionizes CH\textsubscript{2}OH\textsubscript{+} from the well A into (CH\textsubscript{3}⋯OH\textsubscript{2})\textsuperscript{+}, and CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+} from the well B into (CH\textsubscript{2}⋯OH\textsubscript{3})\textsuperscript{+}, which explode into the two singly charged fragment ions in each pathway through the breaking of the C–O bond. Since the C–O bond length in the well A (1.37 Å) is shorter than that in the well B (1.46 Å), the kinetic energy released from the dissociation of (CH\textsubscript{3}⋯OH\textsubscript{2})\textsuperscript{+} is expected to be larger than that from the dissociation of (CH\textsubscript{2}⋯OH\textsubscript{3})\textsuperscript{+}, which is in good agreement with the kinetic energy releases for the nonmigrated (5.9 eV) and the migrated (5.2 eV) species.

The observation that the peak position of 5.2 eV for the migration pathway shown in the upper strip exhibits a large difference from the pump-only value further reveals the dynamics of the hydrogen migration within a singly charged methanol molecule. The observed pump-only peak positions at 4.9 eV for both the nonmigration and migration pathways indicate that the distance between the two dissociating moieties in the precursor species CH\textsubscript{3}⋯OH\textsuperscript{+} and that in CH\textsubscript{2}⋯OH\textsubscript{2}\textsuperscript{+} does not change so much during the double ionization processes from neutral methanol by a 38-fs laser pulse. Since the Coulomb explosion is considered to occur immediately after the formation of doubly charged CH\textsubscript{3}⋯OH\textsuperscript{+} and CH\textsubscript{2}⋯OH\textsubscript{2}\textsuperscript{+} species, the hydrogen migration should proceed in the singly charged manifold during the period of light-molecule interaction. Therefore, the singly charged (CH\textsubscript{2}⋯OH\textsubscript{3})\textsuperscript{+} can be prepared in the area B’ in Fig. 2, where the C–O distance is close to that in the area A for (CH\textsubscript{3}⋯OH\textsuperscript{+}), rather than in the area around the bound well B.

The observation that the peak position of the kinetic energy distribution in Fig. 1(b) at Δt=100 fs decreases from 5.9 eV to 5.2 eV shows that the C⋯O distance in CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+} is stretched from B’ to B after being irradiated with the pump pulse. In addition, the broader kinetic energy distribution for the upper strip shown in Fig. 1(b) than that in Fig. 1(a) may reflect the preparation of a wave packet of the ground state of neutral methanol onto the repulsive slope of the PES around the area B’.

The calculated energy of the transition state located between CH\textsubscript{3}OH\textsuperscript{+} and CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+} is 1.51 and 1.48 eV higher than the potential minimum around A and that around B, respectively. Therefore, when a methanol molecule is prepared on the PES in the wells of A and B after the pump pulse irradiation, the hydrogen migration would not proceed on the PES because of the barrier separating these two wells, and thus, the relative ion yield obtained from the yield of the nonmigrating pathway (γ\textsubscript{non-mig}) and that of the migration pathway (γ\textsubscript{mig}) with respect to the total ion yield (γ\textsubscript{total}=γ\textsubscript{non-mig}+γ\textsubscript{mig}) defined as η\textsubscript{non-mig}=γ\textsubscript{non-mig}/γ\textsubscript{total}, and η\textsubscript{mig}=γ\textsubscript{mig}/γ\textsubscript{total} are expected to be constant. This is indeed the case as observed in our experiment. In Figs. 3(a) and 3(b), η\textsubscript{non-mig} and η\textsubscript{mig} are plotted as a function of the time delay for the upper strips shown in Figs. 1(a) and 1(b) with E\textsubscript{kin} >3.8 eV. It can be seen that the yield ratios, η\textsubscript{non-mig} and η\textsubscript{mig}, are independent of the time delay between the pump and the probe pulses.

Contrary, η\textsubscript{non-mig} and η\textsubscript{mig} plotted in Figs. 3(c) and 3(d) for the lower strips shown in Figs. 1(a) and 1(b) with E\textsubscript{kin} ≤3.8 eV exhibit clear temporal change. As the time delay increases, η\textsubscript{non-mig} in Fig. 3(c) decreases, but η\textsubscript{mig} in Fig. 3(d) increases, showing that the hydrogen migration proceeds even after molecules interact with the intense laser field. The time constant for this postlaser pulse hydrogen migration is evaluated to be ~150(50)fs from the exponential fittings to the experimental data, as shown by the solid lines in Figs. 3(c) and 3(d).

The C–O bond energy is calculated to be ~3.2 eV for both CH\textsubscript{3}OH\textsuperscript{+} and CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+}, which is much higher than the height of the barrier (~1.5 eV) for the migration reactions between CH\textsubscript{3}OH\textsuperscript{+} and CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+}. Therefore, once CH\textsubscript{3}OH\textsuperscript{+} and CH\textsubscript{2}OH\textsubscript{2}\textsuperscript{+} are prepared by the first pulse in the energy range above the threshold for the dissociation along the C–O bond, thus also above the barrier for the hydrogen migration, the postlaser pulse hydrogen migration can also proceed.

As can be seen in Fig. 1(a) and 1(b), the signal intensities become weaker when the time delay increases, and the decay constants for both the nonmigration and migration pathways are determined to be ~185(50)fs, indicating that the IVR rates for the migration and nonmigration pathways are almost the same. This decay process, slower than the postpulse migration can be ascribed to the energy dissipation through intramolecular vibrational energy distribution (IVR) processes proceeding in the course of the C–O bond breaking to decrease the probability distribution of the dissociating wave packet moving along the C–O bond stretch for both nonmigration and migration pathways.
In summary, we observed the intense light-field induced hydrogen migration in singly charged stage of methanol, and identified for the first time the two distinctively different time scales of the migration of one hydrogen atom (or a proton), that is, the ultrafast migration occurring within the ultrashort laser field (~38 fs), and the slower postpulse migration (~150 fs) occurring after the light-matter interaction.

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