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Communication: Long-lived neutral H$_2$ in hydrogen migration within methanol dication

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The ejection of triatomic hydrogen molecular ions HD$_2^+$ and D$_3^+$ from CD$_3$OH^{2+} is investigated by first-principle molecular dynamics simulation. Two C–D chemical bonds are found to be broken to form a neutral D$_2$ moiety that vibrates, rotates, and moves for a relatively long period of time (20–330 fs) towards a transition state leading to the ejection of HD$_2^+$ or D$_3^+$. The formation of such a long-lived neutral D$_2$ moiety within a hydrocarbon molecule interprets well the recent experimental findings of the long lifetime of doubly charged energized hydrocarbon molecules prior to the ejection of H$_3^+$. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4830397]

When hydrocarbon molecules are exposed to an intense laser field whose field intensity exceeds $\sim 10^{13}$ W/cm^2, a variety of dynamical processes are induced such as multiple ionization, chemical bond rearrangement, and Coulomb explosion. Among them, a hydrogen migration process within a hydrocarbon molecule, leading to large-scale chemical bond rearrangement processes, has been known as one of the most characteristic dynamics of molecules induced by an intense laser field.[1]

It was revealed from our experimental study[2] that a triatomic hydrogen molecular ion H$_3^+$ is produced from the two-body Coulomb explosion process of methanol dication CH$_3$OH^{2+}. This observation shows that at least three C–H chemical bonds are broken and new three H–H chemical bonds are formed prior to the two-body Coulomb explosion into H$_3^+$ and CHO$^+$. Furthermore, it was shown from the observed isotropic angular distribution of H$_3^+$ that the formation of H$_3^+$ is a very slow process whose time scale is comparable with or even longer than the overall rotational motion of a parent dication ($\sim$ps). It was further revealed that triatomic hydrogen molecular ions D$_3^+$ and HD$_2^+$ are produced from a partially deuterated methanol dication CD$_3$OH^{2+}. The observation of the H/D mixed triatomic hydrogen molecular ion HD$_2^+$ shows that the hydrogen migration should have proceeded in the formation of the triatomic hydrogen molecular ion from methanol dication.

In the present study, in order to clarify the mechanism of the formation of the triatomic hydrogen molecular ion from methanol dication, we investigate theoretically the temporal evolution of the geometrical structure and the charge distribution of CD$_3$OH^{2+}, and find that a neutral D$_2$ appearing within CD$_3$OH^{2+} plays a central role in the migration and exchange of H and D atoms prior to the formation of D$_3^+$ and HD$_2^+$.

We calculated first-principles molecular dynamics trajectories on the potential energy surface of the adiabatic ground

state of CD$_3$OH^{2+} using the velocity Verlet method.[3] The adiabatic potential energy and its gradients with respect to the nuclear displacements are computed on the fly by using GAUSSIAN09 programs at the CISD/6-311G(2d,p) level of theory.[4] An ensemble of geometrical structures of neutral CD$_3$OH with initial velocities of the respective nuclei at 300 K are adopted as the initial conditions of the first-principle molecular dynamics calculation on CD$_3$OH^{2+} by assuming that CD$_3$OH^{2+} is prepared in its electronic ground state by instantaneous ionization. When CD$_3$OH^{2+} is prepared in an intense laser field, its geometrical structure may be deformed. However, considering that the formation of triatomic hydrogen molecular ions has also been observed when doubly charged methanol is prepared by soft X-ray irradiation[5] as well as by electron impact ionization,[5,6] the present dynamical calculations starting from the geometry of neutral CD$_3$OH are expected to show us essential aspects of the nuclear dynamics leading to the formation of D$_3^+$ and HD$_2^+$.

The ensemble is computed by the Metropolis sampling method.[7] The time step Δt is set to be $\Delta t = 0.1$ fs, and the simulation is performed until $t = 1$ ps. The criterion of the total energy conservation is set to be 10^{-4} Hartree. When one of the internuclear distances within CD$_3$OH^{2+} exceeds 10 Å in a trajectory, it is judged that the dissociation is completed. A total of 1000 trajectories were calculated.

The calculated relative yields of the decomposition pathways are summarized in Table I. With the present initial ensemble, a total of five different two-body decomposition pathways and two different three-body decomposition pathways are identified. The major decomposition pathway is the ejection of D$^+$ from CD$_3$ group whose relative yield is 67.6%. The decomposition pathway with the second largest yield is the ejection of D$_3^+$ whose relative yield is 13.7%. On the other hand, the yield of the ejection of H$^+$ from the hydroxyl group is 0.4% and that of the ejection of HD$_2^+$ is 1.6%. The smaller yields of HD$_2^+$ with respect to D$_3^+$, I(HD$_2^+$)/I(D$_3^+$) = 0.12, which is consistent with the observed yield ratios,

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TABLE I. Relative yields of the decomposition pathways of CD_3OH^{2+}.

Final products	Yield (%)
$D^+ + CD_2OH^+$	67.6
$H^+ + CD_2OD^+$	0.4
$D_2 + CDOH^{2+}$	11.9
$D_3^+ + COH^+$	13.7
$HD_2^+ + CDO^+$	1.6
$H^+ + DCO^+ + D_2$	2.8
$D^+ + COH^+ + D_2$	1.3
Hydrogen migration (CD_2OHD^{2+})	0.2
No dissociation, no hydrogen migration	0.5

$I(HD_2^+)/I(D_3^+) = 0.29$ in Ref. 8 and $I(HD_2^+)/I(D_3^+) = 0.20$ in Ref. 9, may reflect the fact that a D_2 moiety produced within the methyl group needs to move much longer distance to form HD_2^+ than the distance to form D_3^+.

The snapshots of one of the typical trajectories in which HD_2^+ is eventually produced are shown in Fig. 1. First, two C–D chemical bonds in the methyl group are broken and a new D–D chemical bond is formed to become a neutral D_2 moiety, as shown in Fig. 1(b). The D_2 moiety picks up an electron deficient H atom from the hydroxyl group, and eventually a triatomic HD_2^+ moiety is formed. In Fig. 2, an example of the snapshots for the D_3^+ formation is shown. Similarly to Fig. 1(b), the formation of a neutral D_2 moiety can be seen in Fig. 2(b). It should be noted that the formation of a neutral D_2 moiety was commonly identified in all the trajectories leading to the formation of HD_2^+ and D_3^+.

For describing the motion of the D_2 moiety formed within CH_3OH^{2+}, we introduce three parameters, $\vec{R}_1$, $\vec{R}_2$, and θ, where $\vec{R}_1$ is the vector from one of the D atoms, D(1), to the other, D(2), that eventually form the D_2 moiety, $\vec{R}_2$ is the vector from the center of the two D atoms to the center of C and O atoms, and the angle θ is the inner angle between $\vec{R}_1$ and $\vec{R}_2$.

The time evolution of $|\vec{R}_1|$, which is the internuclear distance between the two D atoms, and $|\vec{R}_2|$ of one of the trajectories in which HD_2^+ is eventually produced is shown in Fig. 3(a). In the time range between 75 and 230 fs, $|\vec{R}_1|$ vibrates around 0.8 Å and $|\vec{R}_2|$ elongates up to 3.8 Å. The time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ shows that the D_2 moiety survives for a relatively long period of time (75–230 fs), seemingly separated from the rest of the molecule.

Interestingly, as shown in Fig. 3(b), the sum of the atomic charges of the two D atoms ρ_{D2} is found to be very close to zero during the period when the isolated D_2 moiety vibrates and moves towards the hydroxyl group. Then, at $t = 240$ fs, the D_2 moiety picks up the H atom in the hydroxyl group to form an isolated HD_2^+ having the net charge of +1.0.
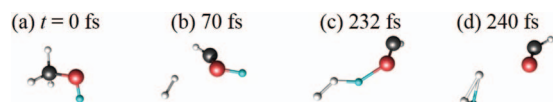
FIG. 1. Snapshots of one of the trajectories for $CD_3OH^{2+} \rightarrow HD_2^+ + CDO^+$. The black, white, red, and blue spheres represent C, D, O, and H atoms, respectively.
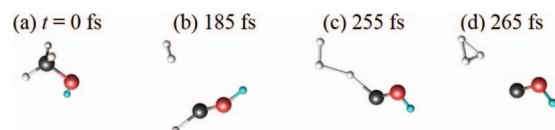
FIG. 2. Snapshots of one of the trajectories for $CD_3OH^{2+} \rightarrow D_3^+ + COH^+$. The black, white, red, and blue spheres represent C, D, O, and H atoms, respectively.

The time propagations of the two distances, $|\vec{R}_1|$ and $|\vec{R}_2|$, and the sum of atomic charges of ρ_{D2} and ρ_{D3}, which is the total charge of three D atoms forming D_3^+ as a final product, are also shown in Fig. 3. The charge ρ_{D2} is close to zero in the period between 150 and 250 fs, and the charge ρ_{D3} of the resultant D_3 moiety has the net charge of +1.0. These results suggest that the formation of a neutral D_2 is a common intermediate step in the hydrogen migration leading to the formation of a triatomic hydrogen molecular ion.

In order to examine in more detail the formation of HD_2^+, the frequency distributions of the cumulative survival time t_{D2} of a neutral D_2 moiety are obtained for the three decomposition pathways, (a) $CD_3OH^{2+} \rightarrow D^+ + CD_2OH^+$, (b) $CD_3OH^{2+} \rightarrow D_3^+ + COH^+$, and (c) $CD_3OH^{2+} \rightarrow HD_2^+ + CDO^+$, and are shown in Fig. 4. In the analysis, a D_2 moiety is regarded as a neutral moiety when (i) the internuclear distance $|\vec{R}_1|$ of the D_2 moiety is $|\vec{R}_1| < 1.1$ Å and (ii) $|\rho_{D2}| \leq 0.2$.

The frequency distribution of t_{D2} for the D^+ ejection pathways is localized in the vicinity of $t_{D2} = 0$ fs. The examination of the trajectories categorized into this pathway shows that D^+ is ejected almost immediately from the methyl group. On the other hand, as shown in Fig. 4(b), t_{D2} for the D_3^+ ejection pathway exhibits a broad frequency distribution peaked at around 40 fs and extending a tail towards the longer time domain. This means that the formation of a neutral D_2
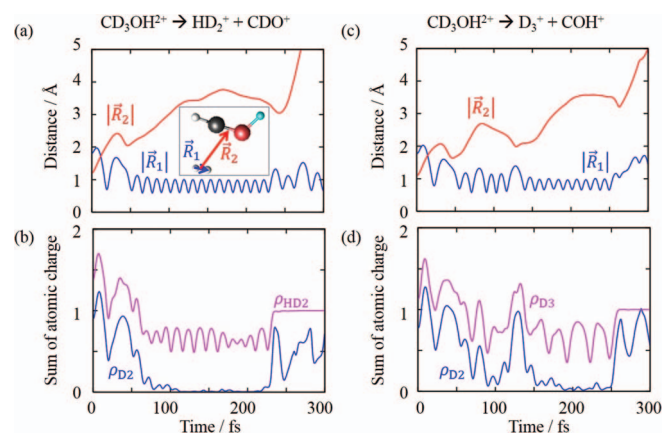
FIG. 3. (a) Time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ for $CD_3OH^{2+} \rightarrow HD_2^+ + CDO^+$, where $|\vec{R}_1|$ is the distance between two D nuclei, and $|\vec{R}_2|$ is the distance between the center of the two D nuclei and the center of the C and O nuclei. The definition of the two vectors $|\vec{R}_1|$ and $|\vec{R}_2|$ is shown in the inset. (b) Time evolution of (i) the sum of the total charge ρ_{D2} of two D atoms forming a neutral D_2 moiety and (ii) the total charge of two D atoms and one H atom forming HD_2^+ as a final product. (c) Time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ for $CD_3OH^{2+} \rightarrow D_3^+ + COH^+$. (d) Time evolution of (i) the sum of the total charge ρ_{D2} of two D atoms forming a neutral D_2 moiety and (ii) the total charge of three D atoms forming D_3^+ as a final product.
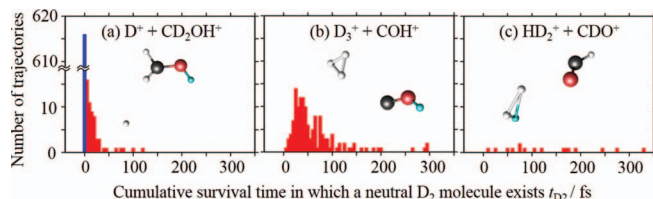
FIG. 4. Frequency distributions of the cumulative survival time t_{D2} of a neutral D_2 moiety for the three decomposition pathways: (a) $CD_3OH^{2+} \rightarrow D^+ + CD_2OH^+$, (b) $CD_3OH^{2+} \rightarrow D_3^+ + COH^+$, and (c) $CD_3OH^{2+} \rightarrow HD_2^+ + CDO^+$. The width of the bin in the histogram is 5 fs.
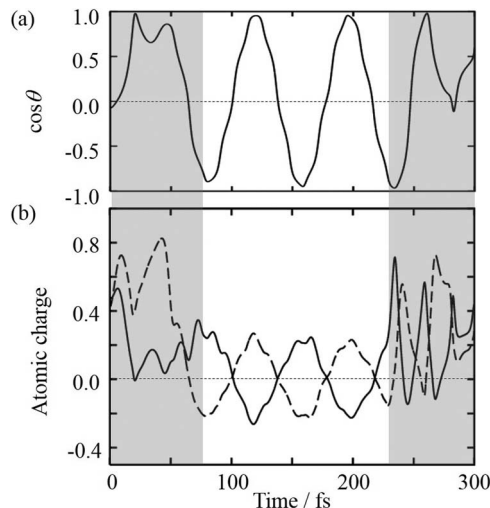

FIG. 5. (a) Time evolution of $\cos\theta$. (b) Time evolution of atomic charges of two D atoms forming a neutral D_2 moiety. The solid and dashed lines indicate the atomic charges of D(1) and D(2), respectively. The time domain between 75 and 230 fs represents the forming of a neutral D_2 moiety.

moiety for a relatively long period of time is prerequisite for the formation of D_3^+. Even though the number of trajectories for the HD_2^+ ejection pathway is not sufficiently large to treat them statistically, the very wide distribution of the cumulative survival probabilities of D_2 in the HD_2^+ pathway shown in Fig. 4(c) shows that the ejection of HD_2^+ is a very slow process as in the formation of D_3^+ shown in Fig. 4(b). It can be said, similarly to the case of the D_3^+ ejection pathway, that HD_2^+ is formed when a neutral D_2 survives for a relatively long period of time.

It is worth investigating how the neutral D_2 vibrates and rotates within CD_3OH^{2+}. We calculate the vibrational frequency of D_2 from the temporal variation of $|\vec{R}_1|$ during the period when the D_2 moiety is regarded as a neutral moiety. The vibration frequency of the D_2 moiety is calculated to be 2980 cm^{-1} from the time evolution of $|\vec{R}_1|$ of Fig. 3(a) and 2765 cm^{-1} from that of Fig. 3(c). Those frequencies are comparable with the experimental fundamental vibrational frequency, 3115 cm^{-1}, of D_2, which is consistent with the idea obtained by the charge analysis that the D_2 moiety can be regarded as an isolated neutral D_2 molecule.

Next, the cosine of the rotational angle θ of the D_2 moiety, defined as $\cos\theta = |\vec{R}_1 \cdot \vec{R}_2|/|\vec{R}_1||\vec{R}_2|$, as well as that of the atomic charges of two D atoms forming the D_2 moiety are plotted as a function of time as shown in Fig. 5 for the same trajectory that was used to draw Figs. 3(a) and 3(b). In the time domain between 75 and 230 fs when a neutral D_2 moiety is formed, the atomic charges of two D atoms oscillate out of phase synchronously with the oscillation of the rotation of the D_2 moiety. This temporal evolution exhibits clearly that when one of the two D atoms in the neutral D_2 moiety becomes closer to the rest of the molecule, that is, the moiety of $CDOH^{2+}$, its charge becomes slightly negative because of the Coulomb attraction, and simultaneously the charge at the other D atom becomes slightly positive so that net charge of the D_2 moiety is balanced to be zero. This means that the charge induced dipole moment is generated in the D_2 moiety, and it is bound with the dication moiety $CDOH^{2+}$ through the attractive interaction between the charge and the charge-induced dipole moment. This characteristic intermolecular-type intramolecular interaction is considered to be the mechanism of keeping the distance between D_2 and $CDOH^{2+}$ long enough so that the neutral D_2 moiety can survive for a long period of time within CD_3OH^{2+}.

In previous theoretical studies, transition states composed of a neutral H_2 moiety leading to the ejection of H_3^+ have been suggested on allene dication[10] and ethane dication.[11]

By contrast, we have shown in the present study the possibility of the existence of a long-lived neutral D_2 (H_2) moiety, which vibrates and rotates before reaching the transition state for the ejection of D_3^+ (H_3^+). In the series of our experimental studies on hydrocarbon molecules such as methanol,[2] cyclohexane,[12] allene,[13] methylacetylene,[14] and ethane,[15] the angular distributions of the fragment ion H_3^+ were reported to be almost isotropic, i.e., the lifetimes of the precursor parent dications leading to the ejection of H_3^+ were found to be comparable with or even longer than the overall rotational motion of the parent dication ($\sim$ps). The mechanism of the existence of energized dication molecules for such a long period of time has been an unsolved issue in these years, but the present theoretical study strongly suggests that the existence of a long lived, vibrating, and rotating H_2 moiety within a dication molecule is the origin to the long lifetime of the dication molecule prior to the ejection of H_3^+.

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