

Long-Lived Neutral H₂ in Hydrogen Migration within Hydrocarbon Dication

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Abstract: First principles molecular dynamics calculations of energized CH₃NH₂²⁺ and CH₃CH₃²⁺ show that a long-lived neutral H₂ moiety is formed within a doubly charged parent ion, leading eventually to the formation of H₃⁺.

OCIS codes: (000.1570) Chemistry, (140.3450) Laser-induced chemistry

1. Introduction

When hydrocarbon molecules are exposed to an intense laser field whose field intensity exceeds $\sim 10^{13}$ W/cm², a variety of dynamical processes are induced such as multiple ionization, chemical bond rearrangement, and Coulomb explosion. In the series of experimental studies on hydrocarbon molecules such as methanol[1] and ethane[2], the angular distributions of the fragment ion H₃⁺ were reported to be almost isotropic, *i.e.*, the lifetimes of the precursor parent dications leading to the ejection of H₃⁺ were found to be comparable with or even longer than the overall rotational motion of the parent dication (\sim ps).

In our recent theoretical study on [3], we performed first-principles molecular dynamics trajectory calculations of energized CH₃OH²⁺ and showed that the formation of a long-lived neutral H₂ moiety within CH₃OH²⁺ can be the origin of the long lifetime of CH₃OH²⁺. In the present study, as an extension of our previous study, we performed the trajectory calculations of energized dication species, CH₃NH₂²⁺ and CH₃CH₃²⁺, and examine if the formation of a long-lived neutral H₂ moiety can commonly be found in these dication species.

2. Theoretical calculations

We calculated first-principles molecular dynamics trajectories on the potential energy surface of the adiabatic ground state of CH₃NH₂²⁺ and CH₃CH₃²⁺ using the velocity Verlet method. The adiabatic potential energy and its gradients with respect to the nuclear displacements are computed on the fly by using GAUSSIAN09 programs at the UCISD/6-311G(2d,p) level. A Wigner distribution of neutral molecules is used as the initial geometrical structures of its dication by assuming that dication is prepared in its electronic ground state by the instantaneous ionization. The time step Δt is set to be $\Delta t = 0.1$ fs, and the simulation is performed until $t = 500$ fs. The criterion of the total energy conservation is set to be 10^{-4} Hartree. When one of the internuclear distances exceeds 10 Å in a trajectory, it is judged that the dissociation is completed.

3. Results and Discussion

The calculated relative yields of the decomposition pathways of CH₃NH₂²⁺ are summarized in Table I. With the present initial ensemble, a total of two different non-decomposition pathways and four different two-body decomposition pathways are identified. One of the non-decomposition pathways is regarded as a hydrogen migration pathway, *i.e.*, a hydrogen atom moves from the methyl group to the amino group. For the H₃⁺ ejection pathways, there are two possible structural isomers, CHNH⁺ and CNH₂⁺, for the counter ion.

The snapshots of one of the typical trajectories in which H₃⁺ and CHNH⁺ are eventually produced are shown in Fig. 1. First, two C-H chemical bonds in the methyl group are broken and a new H-H chemical bond is formed

TABLE I. Relative yields of the decomposition pathways of CH₃NH₂²⁺.

Final products	yield (%)
No dissociation, no hydrogen migration	28.8
Hydrogen migration (CH ₂ NH ₃ ²⁺)	27.4
H ⁺ + CH ₂ NH ₃ ⁺	11.0
H ₂ + CHNH ₂ ²⁺	24.7
H ₃ ⁺ + CHNH ⁺	4.1
H ₃ ⁺ + CNH ₂ ⁺	4.1

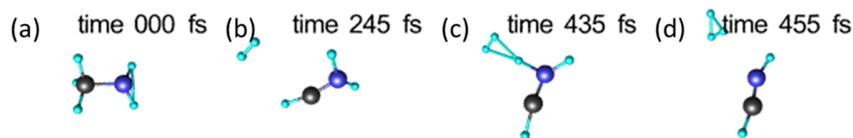


Figure 1. Snapshots of $\text{CH}_3\text{NH}_2^{2+} \rightarrow \text{H}_3^+ + \text{CHNH}^+$. Black, cyan, and blue spheres indicate C, H, and N nuclei, respectively.

to become a neutral H_2 moiety, as shown in Fig. 1(b). Then, the H_2 moiety picks up an electron deficient H atom from the amino group, and eventually, a triatomic H_3^+ moiety is formed.

The time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ of one of the trajectories in which H_3^+ and CHNH^+ are eventually produced is shown in Fig. 2(a). In the time range between 230 and 430 fs, $|\vec{R}_1|$ vibrates with the very small amplitude around 0.75 Å, and $|\vec{R}_2|$ increases to be as large as 4.2 Å. The time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ shows that the H_2 moiety

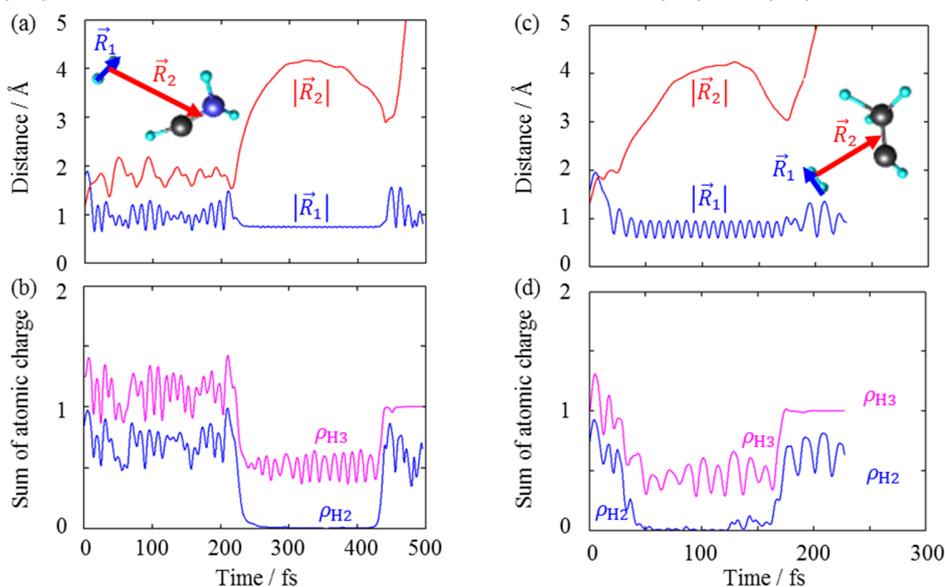


Figure 2. (a) Time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ for $\text{CH}_3\text{NH}_2^{2+} \rightarrow \text{H}_3^+ + \text{CHNH}^+$, where $|\vec{R}_1|$ is the distance between two H nuclei, and $|\vec{R}_2|$ is the distance between the center of the two H nuclei and the center of the C and N nuclei. The definition of the two vectors, \vec{R}_1 and \vec{R}_2 are shown in the inset. (b) Time evolution of (i) the sum of the total charge ρ_{H_2} of two H atoms forming a neutral H_2 moiety and (ii) the total charge of three H atoms forming H_3^+ as a final product. (c) Time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ for $\text{CH}_3\text{CH}_3^{2+} \rightarrow \text{H}_3^+ + \text{CHCH}_2^+$, where $|\vec{R}_1|$ is the distance between two H nuclei, and $|\vec{R}_2|$ is the distance between the center of the two H nuclei and the center of the two C nuclei. The definition of the two vectors, \vec{R}_1 and \vec{R}_2 are shown in the inset. (d) Time evolution of (i) the sum of the total charge ρ_{H_2} of two H atoms forming a neutral H_2 moiety and (ii) the total charge of three H atoms forming H_3^+ as a final product.

survives for a relatively long period of time (230 to 430 fs), seemingly separated from the rest of the molecule.

Interestingly, as shown in Fig. 2(b), the sum of the atomic charges of the two H atoms ρ_{H_2} is found to be very close to zero during the period when the isolated H_2 moiety vibrates and moves toward the amino group. Then, at $t = 430$ fs, the H_2 moiety picks up the H atom in the amino group to form an isolated H_3^+ having the net charge of +1.0.

We plot (i) the time evolution of $|\vec{R}_1|$ and $|\vec{R}_2|$ of one of the trajectories for $\text{CH}_3\text{CH}_3^{2+} \rightarrow \text{H}_3^+ + \text{CHCH}^+$ in Fig. 2(c) and (ii) the time evolution of ρ_{H_2} and ρ_{H_3} denoting respectively the sum of the charges of the two H atoms and that of the three H atoms forming H_3^+ as a final product in Fig. 2(d), which clearly shows a neutral H_2 moiety is also formed in $\text{CH}_3\text{CH}_3^{2+}$. The results obtained for $\text{CH}_3\text{OH}^{2+}$ previously [3] and those obtained in the present study for $\text{CH}_3\text{NH}_2^{2+}$ and $\text{CH}_3\text{CH}_3^{2+}$ suggest that the formation of a long-lived H_2 moiety within a doubly charged hydrocarbon molecule is a universal phenomenon, lengthening its lifetime prior to the ejection of H_3^+ .

[1] T. Okino, Y. Furukawa, P. Liu, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, and H. Nakano, "Coincidence momentum imaging of ultrafast hydrogen migration in methanol and its isotopomers in intense laser fields," *Chem. Phys. Lett.* **423**, 220 (2006).

[2] K. Hoshina, Y. Furukawa, T. Okino, K. Yamanouchi, "Efficient ejection of H_3^+ from hydrocarbon molecules induced by ultrashort intense laser fields," *J. Chem. Phys.* **129**, 104302-1-6 (2008).

[3] K. Nakai, T. Kato, H. Kono, K. Yamanouchi, "Communication: Long-lived neutral H_2 in hydrogen migration within methanol dication," *J. Chem. Phys.* **139**, 181103 (2013).