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Ultrafast hydrogen migration in allene in intense laser fields

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[Introduction]

Ultrafast hydrogen migration in molecules induced by intense laser fields is a chemical-bond rearrangement process that can afford us a new strategy for chemical reaction control [1]. In the present study, using a coincidence momentum imaging (CMI) method, ultrafast hydrogen migration in allene (CH_2CCH_2) induced by a femtosecond intense laser field is investigated. From the CMI maps, we have securely identified two types of the two-body Coulomb explosion pathways of $C_3H_4^{2+} \rightarrow CH_n^+ + C_2H_{4-n}^+$ and $C_3H_4^{2+} \rightarrow H_n^+ + C_3H_{4-n}^+$ (n =1-3). The observation of H_3^+, CH_3^+ and $C_2H_3^+$, ejected from $C_3H_4^{2+}$ confirms that the chemical bond rearrangement through the hydrogen migration occurs prior to the Coulomb explosion.

[Experiments]

The laser pulses (790 nm, 40 fs, 40 μJ), generated by a 5 kHz Ti: Sapphire laser system, were focused through a quartz lens (f =15 cm) onto a sample molecular beam of allene in an ultrahigh vacuum chamber. The laser intensity at the focal spot was $\sim 2\times10^{13}$ W/cm^2. The base pressure of the ultrahigh vacuum chamber is about 8×10^{-11} Torr. In order to avoid false coincidence events originating from the fragment ions generated from two or more parent ions, the pressure in the main chamber was kept to be $\sim 8\times10^{-10}$ Torr, so that the number of events of the generation of ion species per laser shot was ~0.55 events/pulse. The laser polarization direction, electrode plates, and the surface of the detector were all set to be parallel to the plane formed by the laser and molecular beams. The three-dimensional momentum vectors of i-th fragment ions were determined by their position (x_i, y_i) and arrival time (t_i) on the detector plane [2].

[Results and Discussion]

In Fig. 1, the momentum imaging maps of CH_n^+ and H_n^+ (n =1-3), appearing in coincidence respectively with $C_2H_{4-n}^+$ and $C_3H_{4-n}^+$, are illustrated, revealing the six two-body Coulomb explosion pathways through the C-C or C-H bond breaking:

$$CH_2CCH_2^{2+} \rightarrow C_2H_2^+ + CH_2^+ \qquad (1)$$
$$CH_2CCH_2^{2+} \rightarrow C_2H^+ + CH_3^+ \qquad (2)$$
$$CH_2CCH_2^{2+} \rightarrow C_2H_3^+ + CH^+ \qquad (3)$$
$$CH_2CCH_2^{2+} \rightarrow C_3H_3^+ + H^+ \qquad (4)$$
$$CH_2CCH_2^{2+} \rightarrow C_3H_2^+ + H_2^+ \qquad (5)$$
$$CH_2CCH_2^{2+} \rightarrow C_3H^+ + H_3^+ . \qquad (6)$$

The formation of CH_3^+, $C_2H_3^+$ and H_3^+ shows clearly that the migration of one hydrogen atom (or a proton) proceeds within an allene molecule prior to the Coulomb explosion.

From the six observed CMI maps, the values of the extent of anisotropy, $\langle\cos^2\theta\rangle = \int I(\theta)\cos^2\theta\sin\theta d\theta \,/\, \int I(\theta)\sin\theta d\theta$, are obtained as plotted in Fig. 2. These $\langle\cos^2\theta\rangle$ values can be categorized into two groups: (i) CH_n^+, in which C-C bond is broken, and (ii) H_n^+, in which C-H bond is broken. For CH_n^+, the $\langle\cos^2\theta\rangle$ values show a characteristic dependence on the number of hydrogen atoms, n, while the $\langle\cos^2\theta\rangle$ values for H_n^+ exhibit are all small and depend only weakly on n. The $\langle\cos^2\theta\rangle$ values for the three C-H bond breaking pathways are in the range of 0.37-0.39, showing that the angular distributions are more isotropic. This suggests that the precursor species $C_3H_{4-n}^+\cdots H_n^+$ (n = 1-3) from which H_n^+ is ejected are

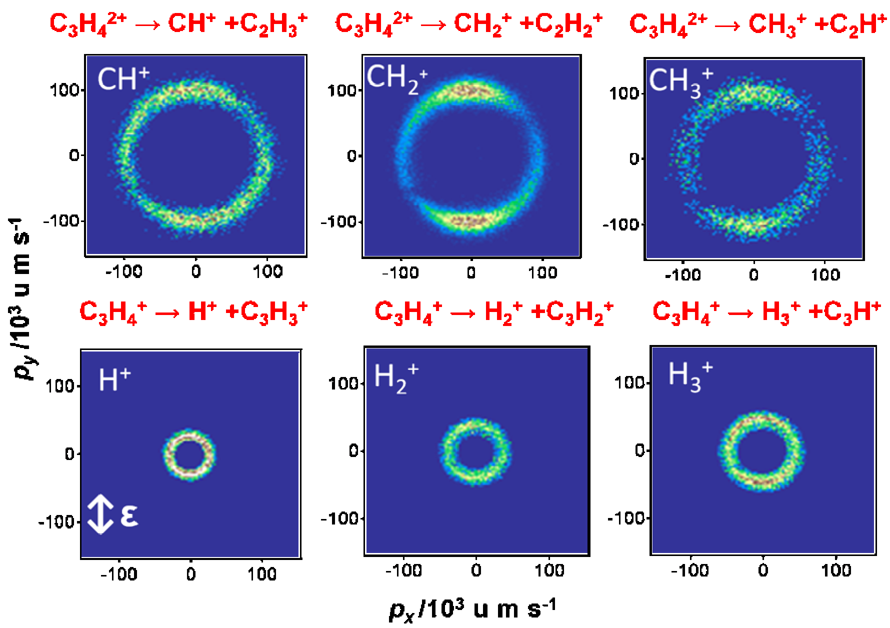

Fig. 1. Observed two-dimensional coincidence momentum maps of CH^+, CH_2^+, CH_3^+, H^+, H_2^+, H_3^+ recorded in coincidence with $C_2H_3^+$, $C_2H_2^+$, C_2H^+, $C_3H_3^+$, $C_3H_2^+$, C_3H^+, through the two-body Coulomb explosion processes of $C_3H_4^{2+}$. The laser polarization direction (ε) is set to be parallel with the p_y axis as indicated by the arrow.

prepared in the metastable quasi-bound area of the potential energy surfaces, and that their dissociation lifetimes are comparable with the rotational period of the parent allene molecule. The relatively large $\langle \cos^2\theta \rangle$ values for the three C-C bond breaking pathways indicate that allene molecules whose C=C=C skeletal axis is directed along the laser polarization direction are doubly ionized efficiently, and that the precursor species $CH_n^+ \cdots C_2H_{4-n}^+$ (n = 1-3) are prepared on the repulsive Coulombic potential energy surfaces so that the two-body Coulomb explosion proceeds more rapidly than the overall molecular rotation. After the formation of $CH_n^+ \cdots C_2H_{4-n}^+$ within the intense laser field, the probability that a hydrogen atom jumps between the two distant moieties, CH_n^+ and $C_2H_{4-n}^+$, may be significantly small. This means that the hydrogen migration is expected to stop prior to the C···C bond breaking. Since the doubly charged precursor species, $CH_n^+ \cdots C_2H_{4-n}^+$, are considered to be produced in the intense laser field, the hydrogen migration processes are expected to proceed within the period of the ultrafast laser pulse (~ 40 fs).

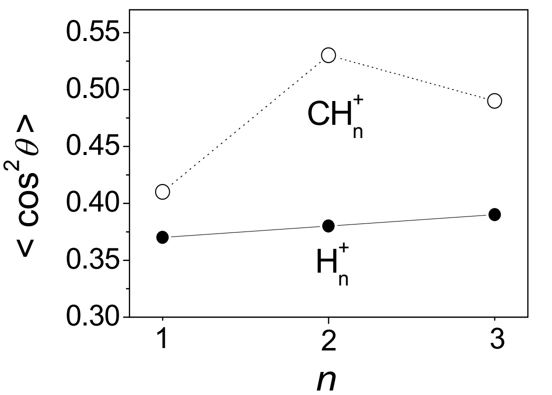

Fig.2. The schematic diagram for the $\langle \cos^2\theta \rangle$ values of the fragment ions, CH_n^+, and H_n^+.

Reference

[1] T. Okino, Y. Furukawa, P. Liu, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, and H. Nakano, Chem. Phys. Lett. **423**, 220 (2006)

[2] H. Hasegawa, A. Hishikawa, and K. Yamanouchi, Chem. Phys. Lett. **349**, 57 (2001)