

# Hydrogen scrambling in $\text{H}_3^+$ generation from ethane induced by ultrashort intense laser fields

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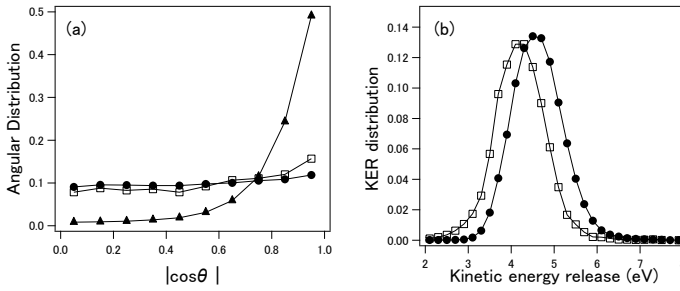
**Abstract.** Two-body Coulomb explosion processes of ethane ( $\text{CH}_3\text{CH}_3$ ) and its isotopomers ( $\text{CD}_3\text{CD}_3$  and  $\text{CH}_3\text{CD}_3$ ) induced by an intense laser field are investigated by a coincidence momentum imaging method. From the yield ratios of  $\text{H}_3^+$ ,  $\text{H}_2\text{D}^+$ ,  $\text{HD}_2^+$ , and  $\text{D}_3^+$  ejected from  $\text{CH}_3\text{CD}_3^+$  induced by an ultrashort-pulsed intense laser field, nearly statistical randomization of H and D atoms called hydrogen atom scrambling was identified.

## 1 Introduction

When hydrocarbon molecules are exposed to an intense laser field, a variety of dynamical processes originating from ultrafast motion of hydrogen atoms proceed such as ultrafast hydrogen migration and ejection of  $\text{H}_3^+$ , as has been shown in our recent studies on methanol [1], ethane [2-4], and other hydrocarbon molecules [2]. In the present study, in order to clarify how hydrogen atoms and/or protons migrate within an ethane molecule and to what extent the hydrogen atoms and protons exchange their positions among each other, we measured coincidence momentum imaging maps of fragment ions produced from ethane exposed to an intense laser field.

## 2 Experimental setup

Ultrashort laser pulses ( $\lambda = 800$  nm,  $I = 1.0 \times 10^{14}$  W/cm<sup>2</sup>,  $\Delta t = 120$  fs, 5 kHz) were introduced into an ultrahigh vacuum chamber ( $7 \times 10^{-11}$  Torr) and focused with a quartz lens ( $f = 150$  mm) at the point where the laser pulses crossed at right angles with a molecular beam of ethane ( $\text{CH}_3\text{CH}_3$ ), ethane-*d*<sub>6</sub> ( $\text{CD}_3\text{CD}_3$ ), or ethane-1,1,1-*d*<sub>3</sub> ( $\text{CH}_3\text{CD}_3$ ). The ions generated at the laser focal spot were projected by four equally spaced parallel-plate electrodes in the velocity mapping configuration onto a position-sensitive detector with delay-line readout. The three-dimensional momentum vectors of the fragment ions were determined by their position and arrival time on the detector plane. The laser polarization direction was set to be parallel to the detector plane. The false coincidence events



**Fig. 1.** (a) Angular distributions and (b) KER distributions of the fragment ions generated from the Coulomb explosions of  $\text{CH}_3\text{CD}_3^{2+}$  and  $\text{C}_2\text{H}_6^{2+}$ . Filled triangles:  $\text{CH}_3\text{CD}_3^{2+} \rightarrow \text{CH}_3^+ + \text{CD}_3^+$ , Filled circles:  $\text{C}_2\text{H}_6^{2+} \rightarrow \text{H}_3^+ + \text{C}_2\text{H}_3^+$ , Open squares:  $\text{C}_2\text{H}_6^{2+} \rightarrow \text{H}_2^+ + \text{C}_2\text{H}_4^+$ . The angle  $\theta$  is the angle between the laser polarization vector and the momentum vector of the fragment ions.

**Table 1.** The  $\chi$  values for the decomposition pathways of doubly charged ethane.

$M_1$	$M_2$	Pathway	$\chi$
2	28	$\text{C}_2\text{H}_6^{2+} \rightarrow \text{H}_2^+ + \text{C}_2\text{H}_4^+$	0.106
4	32	$\text{C}_2\text{D}_6^{2+} \rightarrow \text{D}_2^+ + \text{C}_2\text{D}_4^+$	0.130
3	27	$\text{C}_2\text{H}_6^{2+} \rightarrow \text{H}_3^+ + \text{C}_2\text{H}_3^+$	0.714
6	30	$\text{C}_2\text{D}_6^{2+} \rightarrow \text{D}_3^+ + \text{C}_2\text{D}_3^+$	0.786
5	28	$\text{C}_2\text{H}_3\text{D}_3^{2+} \rightarrow \text{HD}_2^+ + \text{C}_2\text{H}_2\text{D}^+$	0.834
6	27	$\text{C}_2\text{H}_3\text{D}_3^{2+} \rightarrow \text{D}_3^+ + \text{C}_2\text{H}_3^+$	0.785
3	30	$\text{C}_2\text{H}_3\text{D}_3^{2+} \rightarrow \text{HD}^+ + \text{C}_2\text{H}_2\text{D}_2^+$	0.363
		$\text{C}_2\text{H}_3\text{D}_3^{2+} \rightarrow \text{H}_3^+ + \text{C}_2\text{D}_3^+$	
4	29	$\text{C}_2\text{H}_3\text{D}_3^{2+} \rightarrow \text{D}_2^+ + \text{C}_2\text{H}_3\text{D}^+$	0.698
		$\text{C}_2\text{H}_3\text{D}_3^{2+} \rightarrow \text{H}_2\text{D}^+ + \text{C}_2\text{HD}_2^+$	

originating from two or more parent molecular ions were discriminated from the true coincidence events by imposing the momentum conservation conditions. Furthermore, the probabilities of accidental momentum conservation were estimated from the momentum distributions of the fragment ions, and were taken into account in the data analysis.

## 2 Result & Discussion

The filled triangles in Figure 1(a) show the angular distribution of the momentum vector of  $\text{CH}_3^+$  ions generated through  $\text{CH}_3\text{CD}_3^{2+} \rightarrow \text{CH}_3^+ + \text{CD}_3^+$  with respect to the laser polarization vector. The  $\text{CH}_3^+$  ions are ejected preferentially to the direction of the laser polarization vector ( $\theta = 0$  degree), showing that the  $\text{CH}_3\text{CD}_3^{2+}$  is produced preferentially when the C-C bond is parallel to the laser polarization vector, and that the C-C bond is immediately broken before the overall rotation of  $\text{CH}_3\text{CD}_3^{2+}$  proceeds. On the other hand, the filled circles in Figure 1(a) show the angular distribution of the momentum vector of  $\text{H}_3^+$  ions generated through  $\text{C}_2\text{H}_6^{2+} \rightarrow \text{H}_3^+ + \text{C}_2\text{H}_3^+$ . The obtained isotropic distribution shows that the lifetime of the precursor parent ion,  $\text{C}_2\text{H}_6^{2+}$ , is much longer than the period of the overall molecular rotation,  $\sim 1.6$  ps. In the pathway yielding  $\text{H}_2^+ + \text{C}_2\text{H}_4^+$ , the angular distribution, plotted with the open squares in Figure 1(a), is almost isotropic, but exhibits weak preference along the laser polarization direction. The filled circles and the open squares in Figure 1(b) show the kinetic energy release (KER) of  $\text{H}_3^+ + \text{C}_2\text{H}_3^+$  and  $\text{H}_2^+ + \text{C}_2\text{H}_4^+$  pathways, respectively. No significant differences can be found in these KER distributions. However, the peak position of the  $\text{H}_3^+$  pathway is higher than that of the  $\text{H}_2^+$  pathway by 0.4 eV. The corresponding angular distributions and KER distributions obtained for  $\text{CD}_3\text{CD}_3$  and  $\text{CH}_3\text{CD}_3$  are similar to those obtained for  $\text{CH}_3\text{CH}_3$ .

From the measurements of the decomposition processes of partially deuterated ethane,  $\text{CH}_3\text{CD}_3^{2+}$ , the H-D mixing can be investigated, but the reaction pathway yielding  $\text{H}_3^+ + \text{C}_2\text{D}_3^+$  and those yielding  $\text{HD}^+ + \text{C}_2\text{H}_2\text{D}_2^+$  could not be discriminated from each other because the masses of the fragment ions in both of the reaction pathways are the same, that is, " $M_1 = 3$  and  $M_2 = 30$ ". Similarly, the two reactions  $\text{H}_2\text{D}^+ + \text{C}_2\text{HD}_2^+$  and  $\text{D}_2^+ + \text{C}_2\text{H}_3\text{D}^+$  generate the fragments with the same masses, " $M_1 = 4$  and  $M_2 = 29$ ". It may be possible to derive the relative yields of the two pathways yielding the same mass pair by taking advantage of the differences between their angular distributions and/or KER distributions, but these differences were found to be too small for both cases of " $M_1 = 3, M_2 = 30$ " and " $M_1 = 4, M_2 = 29$ ". Therefore, in order to obtain the yield ratios of  $\text{H}_3^+ : \text{H}_2\text{D}^+ : \text{HD}_2^+ : \text{D}_3^+$ , it was necessary to introduce a new statistical treatment of the coincidence data.

Table 1 shows the ratios defined as  $\chi = N_t / N_c$ , where  $N_t$  is the number of the true coincidence events and  $N_c$  is the event number when the fragment ion and its counterpart ion are detected at the same time. Because the  $\chi$  values for  $\text{H}_2^+ + \text{C}_2\text{H}_4^+$  and  $\text{D}_2^+ + \text{C}_2\text{D}_4^+$  are 0.106 and 0.130, respectively, the  $\chi$  values for  $\text{HD}^+ + \text{C}_2\text{H}_2\text{D}_2^+$  and  $\text{D}_2^+ + \text{C}_2\text{H}_3\text{D}^+$  are expected to take similar values. Considering the average and the standard deviation, the  $\chi$  values for  $\text{HD}^+ + \text{C}_2\text{H}_2\text{D}_2^+$  and  $\text{D}_2^+ + \text{C}_2\text{H}_3\text{D}^+$  are estimated to be  $0.118 \pm 0.017$ . Similarly, from the results of  $\text{H}_3^+ + \text{C}_2\text{H}_3^+$ ,  $\text{D}_3^+ + \text{C}_2\text{D}_3^+$ ,  $\text{HD}_2^+ + \text{C}_2\text{H}_2\text{D}^+$ , and  $\text{D}_3^+ + \text{C}_2\text{H}_3^+$ , the  $\chi$  values for  $\text{H}_3^+ + \text{C}_2\text{D}_3^+$  and  $\text{H}_2\text{D}^+ + \text{C}_2\text{HD}_2^+$  are expected to be  $0.780 \pm 0.050$ . For the mass pairs of " $M_1 = 3$  and  $M_2 = 30$ " and " $M_1 = 4$  and  $M_2 = 29$ ", the  $\chi$  values are obtained to be 0.363 and 0.698, respectively. From these  $\chi$  values, the relative yields of the two pathways are derived for both of the mass pairs, and consequently, the yield ratio of the triatomic hydrogen molecular ions is determined to be  $\text{H}_3^+ : \text{H}_2\text{D}^+ : \text{HD}_2^+ : \text{D}_3^+ = (8.01 \pm 1.20) : (43.0 \pm 5.4) : (43.1 \pm 0.3) : (5.89 \pm 0.10)$ , where the sum of the ratios is 100.

It can be seen from the obtained yield ratio that the yields of  $\text{H}_2\text{D}^+$  and  $\text{HD}_2^+$  are much higher than those of  $\text{H}_3^+$  and  $\text{D}_3^+$ , showing that the H-D scrambling is quite efficient in the pathways from which the triatomic hydrogen molecule is produced. It should be noted that the obtained yield ratio is close to  $\text{H}_3^+ : \text{H}_2\text{D}^+ : \text{HD}_2^+ : \text{D}_3^+ = 5 : 45 : 45 : 5$ , which corresponds to the limit of a random sampling of three H or D atoms from the mixture of three H atoms and three D atoms. This significant H-D scrambling can be regarded as an evidence of energy randomization within a long-lived doubly charged parent ions  $\text{C}_2\text{H}_6^{2+}$ . Furthermore, several theoretical studies reported that the most stable structure of  $\text{C}_2\text{H}_6^{2+}$  takes the carbenium-carbonium dication structure ( $\text{H}_2\text{C}^+ - \text{CH}_4^+$ ) [4-6]. Therefore, it is possible that the stable positions of H/D atoms  $\text{C}_2\text{H}_6^{2+}$ , largely different from neutral ethane, induces efficiently the H-D scrambling in the electronic ground state of  $\text{C}_2\text{H}_3\text{D}_3^{2+}$ .

On the other hand, the analysis of our coincidence data showed that the C-C bond breaking proceeds almost exclusively through the pathway of  $\text{CH}_3\text{CD}_3^{2+} \rightarrow \text{CH}_3^+ + \text{CD}_3^+$  and that the yields of the C-C bond breaking accompanied by H/D migration such as  $\text{CH}_3\text{CD}_3^{2+} \rightarrow \text{CH}_2\text{D}^+ + \text{CHD}_2^+$  and  $\text{CH}_3\text{CD}_3^{2+} \rightarrow \text{CH}_2^+ + \text{CHD}_3^+$  were found to be negligibly small, suggesting that the C-C bond breaking is a much faster process than the H/D migration. These observations are consistent with the highly anisotropic angular distribution of  $\text{CH}_3^+$  generated through  $\text{CH}_3\text{CD}_3^{2+} \rightarrow \text{CH}_3^+ + \text{CD}_3^+$  [Figure 1(a)].

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