

# Identification of the Roaming Mechanism and the Formation of $\text{H}_3^+$ in Core Ionised Cyclopropane

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## 1 Alternative fragments momentum analysis

Fig. S1 shows the momentum distributions of two fragmentation pairs from the dication  $\text{C}_3\text{H}_4^{2+}$  where roaming is not observed. Fig. S1(a) depicts a typical concerted dissociation with a neutral particle; the momentum is split evenly between the charged particles with very little momentum given to the neutral particle. The concerted assignment is further evident by the almost  $180^\circ$  angle between the two charged fragments in Fig. S1(c). Similarly, for the other fragment pair that includes a C-C bond break,  $\text{CH}^+/\text{C}_2\text{H}_3^+$ , from the dication  $\text{C}_3\text{H}_4^{2+}$ , an identical momentum distribution is found to what is shown in Fig. S1(a-c). Fig. S1(d) shows a similar distribution, but slightly shifted towards higher  $\text{C}_3\text{H}_2^+$  momentum. This is attributed to an asynchronous concerted dissociation.

## 2 Confirmation of neutral fragment

As we investigate the fragmentation channel  $\text{H}^+/\text{H}_2/\text{C}_3\text{H}_3^+$  we must confirm that we are not looking at products of the triply charged fragmentation channel  $\text{H}^+/\text{H}_2^+/\text{C}_3\text{H}_3^+$  and our detector misses the charged  $\text{H}_2^+$ . Fig. S2(c) shows that for the triply charged fragmentation there are two peaks for  $\text{H}^+$  and  $\text{H}_2^+$  at 3 and 7 eV. More importantly both of those peaks have an equal intensity for each of the two fragments. In Fig. S2(b) we see only one apparent peak for  $\text{H}^+$  at around 3 eV. If  $\text{H}_2$  in this latter pathway would have been charged we would have expected to see a second peak at 7 eV for the  $\text{H}^+$  as well. Thus, we can conclude that the channel that we are investigating, contains a neutral  $\text{H}_2$  fragment.

## 3 Total KER determination

In the pair  $\text{H}_3^+/\text{C}_3\text{H}_3^+$  we have the kinetic energy of each charged particle and can therefore get the  $\text{KER}_{\text{H}_3^+/\text{C}_3\text{H}_3^+}$ . This is equal to the total KER as it is a complete fragmentation. In the main text a new total KER is introduced

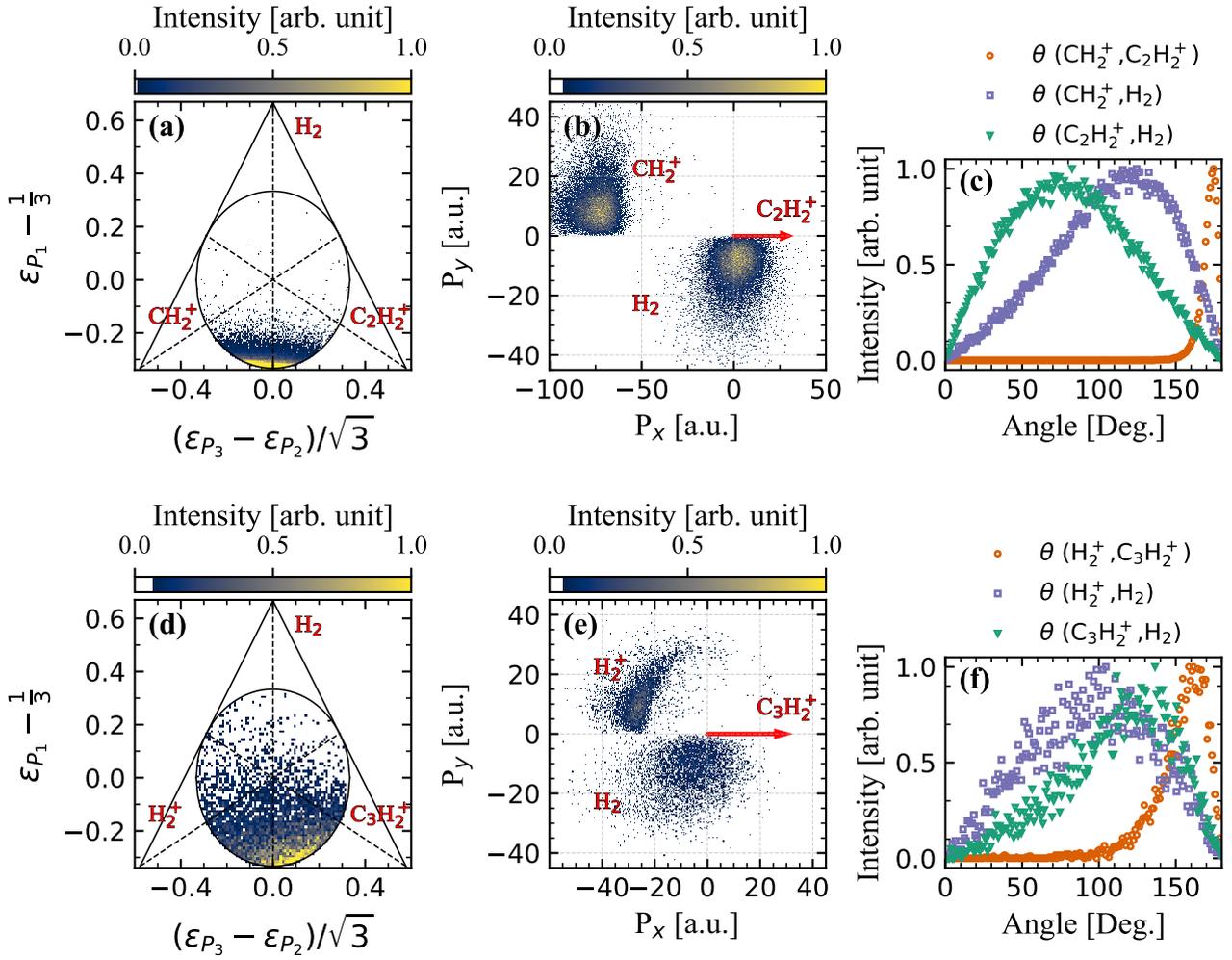


Figure S 1: The momentum vector distribution from the fragmentation channel (a-c)  $\text{H}_2/\text{CH}_2^+/\text{C}_2\text{H}_2^+$  and (d-f)  $\text{H}_2/\text{H}_2^+/\text{C}_3\text{H}_2^+$ . Full description for the sub-figures in the main text.

to compare with the  $\text{H}^+/\text{H}_2/\text{C}_3\text{H}_3^+$  fragments. This total KER takes the  $\text{KER}_{\text{H}_3^+/\text{C}_3\text{H}_3^+}$  and adds the bond energy between  $\text{H}_2$  and  $\text{H}^+$ , of 4.3489 eV. Fig S3 shows the calculated energies; where the bond energy has been broadened by a Gaussian distribution to reflect the experimental resolution of the spectrometer. This broadening also incorporates the possible internal energies not accounted for by just added a single energy, and makes the exact added value less sensitive to external (to the bond) factors. The counts of  $\text{H}_3^+/\text{C}_3\text{H}_3^+$  are not altered.

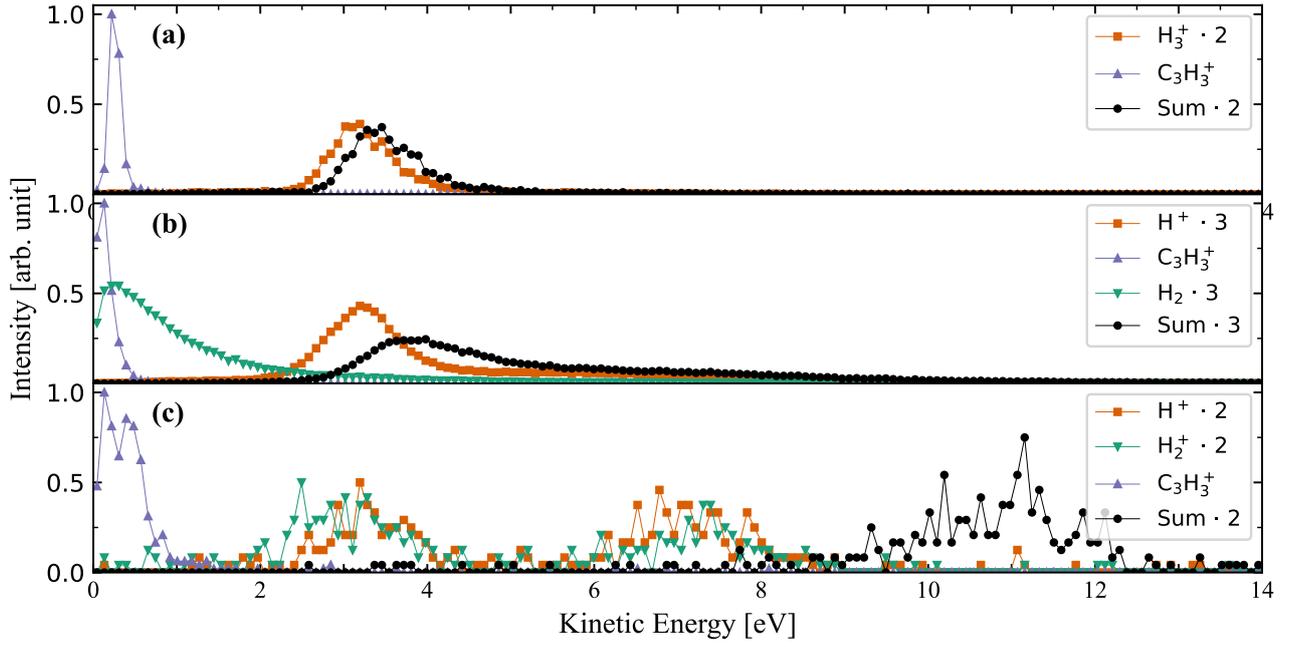


Figure S 2: The kinetic energy of all particles in three different channels, (a)  $H_3^+/C_3H_3^+$ , (b)  $H^+/H_2/C_3H_3^+$  and (c)  $H^+/H_2^+/C_3H_3^+$ . The sum is also shown.

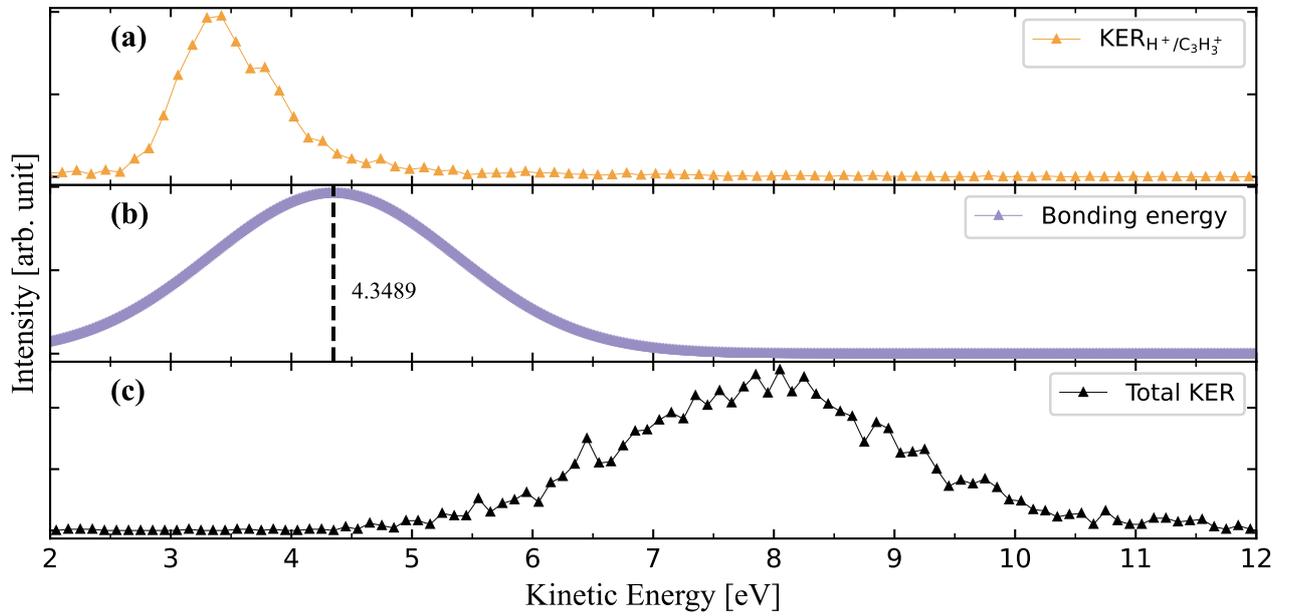


Figure S 3: Kinetic energy of the  $H_3^+/C_3H_3^+$  fragmentation. (a) The  $KER_{H^+/C_3H_3^+}$  can be compared with (b) the calculated bonding energy of  $H_2$  and  $H^+$  and (c) the combined total KER.