Supplementary information

Formation of $\text{H}_3^+$ from Ethane Dication Induced by Electron Impact

Yu Zhang, Baihui Ren, Chuan-Lu Yang, Long Wei, Bo Wang, Jie Han, Wandong Yu, Yue Ying Qi,
Yaming Zou, Li Chen, Enliang Wang, and Baoren Wei

Supplementary Note 1. Coincidence TOF map and ion yields

Coincidence channels are identified through the ion-ion coincidence time-of-flight (TOF) map, i.e. a density plot of the TOF of the first ion vs that of the second one. Supplementary Figure 1 shows the full coincidence TOF map for dissociation of ethane dications. In addition to the interested channels $\text{H}_n^+ + \text{C}_2\text{H}_6$ (n=1-3), there are many other fragmentation channels involving C-H or C-C bond breakages. The counts of all of these channels are estimated in Supplementary Table 1. For the C-C bond-breakage channels, the coincidence stripes are partly overlapped, so particular care should be taken when counting the number. Following Supplementary Table 1, branching ratios among the $\text{H}_n^+$ ions and two-body $\text{H}_n^+$ channels produced by the dissociation of $\text{C}_2\text{H}_6^{2+}$ dications are estimated in Supplementary Table 2.

Supplementary Figure 1. Full ion-ion coincidence TOF map for the dissociation of $\text{C}_2\text{H}_6^{2+}$ dications induced by 300 eV electron impact. The inset is an enlarged spectrum for ion-pairs where the C-C bond of $\text{C}_2\text{H}_6^{2+}$ was broken.
Supplementary Table 1. Number of counts of ion-pairs formed by the dissociation of C$_2$H$_6^{2+}$ dications.

| 1$^{st}$ ion | 2$^{nd}$ ion | H$^+$ | H$_2^+$ | H$_3^+$ | C$^+$ | CH$^+$ | CH$_2^+$ | CH$_3^+$ |
|-------------|-------------|-------|--------|--------|-------|--------|---------|---------|
| C$_2$H$_5^+$ | 711         |       |        |        |       |        |         | 2496    |
| C$_2$H$_4^+$ | 14121       | 16743 |        |        |       |        |         |         |
| C$_2$H$_3^+$ | 98814       | 48834 | 46943  |        |       |        |         |         |
| C$_2$H$_2^+$ | 86439       | 27154 | 10656  |        |       |        |         |         |
| C$_2^+$      | 45825       | 3986  | 352    |        |       |        |         |         |
| CH$_3^+$     | 20843       | 1049  | 29     |        | C$^+$ | 839    | /       | /       |
| H$_3^+$      | 67853       | 2727  | 248    |        |       |        |         |         |
| H$_2^+$      | 2314        | 81    | 22     |        |       |        |         |         |
| H$^+$        | 16088       | 433   | /      |        |       |        |         |         |
|              | 76070       | /     | /      |        |       |        |         |         |

Supplementary Table 2. Branching ratios among the H$_n^+$ ions and two-body H$_n^+$ channels produced by the dissociation of C$_2$H$_6^{2+}$ dications in the present and previous studies.

| H$_n^+$ ion | Present | Intense laser Ref. [1] | 200 eV e$^-$ Ref. [2] | 580 keV C$^+$ Ref. [3] | 200 eV e$^-$ + CH$_4$ Ref. [2] |
|-------------|---------|------------------------|------------------------|------------------------|-------------------------------|
| H$^+$       | 76.0    | 65/64                  | 82.3                   | ~79                    | 96.31                         |
| H$_2^+$     | 15.3    | 20/15                  | 11.6                   | ~14                    | 3.67                          |
| H$_3^+$     | 8.7     | 15/21                  | 6.1                    | ~7                     | 0.02                          |
| Two-body H$_n^+$ channel | Present | Intense laser Ref. [4] | 200 eV e$^-$ Ref. [2] | 300 eV e$^-$ + C$_2$H$_4$ Ref. [5] | 300 eV e$^-$ + CH$_4$ Ref. [5] |
| H$^+$ + C$_2$H$_5^+$ | 1.1     | ~5                     | 0                      | 78.30                  | 79.07                         |
| H$_2^+$ + C$_2$H$_4^+$ | 26.0   | ~7                     | 26.2                   | 21.21                  | 20.73                         |
| H$_3^+$ + C$_2$H$_3^+$ | 72.9   | ~88                    | 73.8                   | 0.49                   | 0.20                          |

Supplementary Note 2. Theoretical channel yields

Note that in the present study we just simulated the dissociation dynamics of ethane dication in the ground state, which has been proven crucial to the formation of H$_3^+$ ions. A total of 1000 trajectories was computed and 230 out of them showed H$_3^+$ formation. The simulation results at 500 fs showed that H$_2$ is produced with fractional charge (mostly 0.5e). Thus the channels ending up with H$_2$ (might in neutral and charge states) correspond to H$_2^+$ + C$_2$H$_4^+$ and H$_2$ + C$_2$H$_2^{2+}$ dissociation limit. In electron-molecule collisions, the ethane dication could be populated in different states, which favor different dissociation channels. Therefore
as shown in Supplementary Table 3 the present theoretical branching ratios extracted from the simulation for ground state do not agree well with the experimental ones.

**Supplementary Table 3. Number of trajectories and branching ratios (BRs) of the two-body H₃⁺ dissociation channels of C₂H₆⁺ dication.**

| Channel | Number of trajectories | Theoretical BR (%) | Experimental BR (%) |
|---------|------------------------|-------------------|---------------------|
| H⁺ + C₂H₅⁺ | 64                      | 6.4               | 1.1                |
| H₂⁺ + C₂H₄⁺ and H₂ +C₂H₄⁺²⁺ | 531                  | 53.1              | 26.0*              |
| H₃⁺ + C₂H₃⁺ | 230                    | 23.0              | 72.9               |

* Only for the H₂⁺ + C₂H₄⁺ channel

**Supplementary Note 3. Theoretical KER for different H₃⁺ formation pathways**

The simulated kinetic energy release (KER) is obtained as follows: (i) calculate the linear momentum and kinetic energy of every subunit, then (ii) sum their kinetic energies to produce the KER, and (iii) add up the remaining Coulomb potential energy of two charged units to obtain the final KER. The KER distributions for different H₃⁺ formation pathways (i.e. transition state, and roaming mechanisms) are shown in Supplementary Figure 2.

**Supplementary Figure 2. KER distribution for different H₃⁺ formation pathways.**

**Supplementary References**

[1] K. Hoshina et al, J. Chem. Phys. 134, 064324 (2011).

[2] P. Wang and C. R. Vidal, Chem. Phys. 280, 309 (2002).

[3] T. Majima et al, Phys. Rev. A 90, 062711 (2014).

[4] R. Kanya et al, J. Chem. Phys. 136, 204309 (2012).

[5] Y. Zhang et al, Phys. Rev. A 100, 052706 (2019).