

Kinetic energy distributions of the fragment ions from multiply ionized C₂H₆ as functions of the charge state of the intermediate states

S. Yoshida^a, T. Majima^{a*}, H. Tsuchida^b, and M. Saito^a

^a *Department of Nuclear Engineering, Kyoto University, Kyoto 606-8501, Japan*

^b *Quantum Science and Engineering Center, Kyoto University, Uji 611-0011, Japan*

*Corresponding author: majima@nucleng.kyoto-u.ac.jp

Abstract

Here, we report the kinetic energy distributions (KEDs) of the fragment ions produced from multiply ionized ethane (C₂H₆) molecules in single electron capture collisions with 1.2 MeV C²⁺. To systematically investigate the fragmentation dynamics, the KEDs were obtained as functions of the charge state of the intermediate C₂H₆^{r+*} ions r transiently generated prior to fragmentation. r was determined from coincidence measurement of the fragment ions and the number of emitted electrons. The KEDs are drastically different depending on the number of broken C–H bonds. The underlying causes are explained by the variation of the relative contributions of the multiply ionized states and preferential fragmentation pathways. For instance, CH _{n} ⁺ fragment ions with smaller n exhibit lower KEs because they are likely to be correlated with H⁺ emission, which

carries away a large portion of the KE release. In addition, we report the KEDs of H_3^+ produced from doubly and triply charged states.

Keywords: molecular fragmentation; multiple ionization; fast ion collisions, kinetic energy distributions, ethane

1. Introduction

Multiple ionization of molecules is induced by strong electric fields generated by intense short laser pulses, collisions of highly charged ions, and swift heavy ions.^[1–3] Highly ionized molecules dissociate or “Coulomb explode” into fragments with high kinetic energies (KEs). Understanding the fragmentation mechanisms is of fundamental interest in molecular sciences and related fields, such as radiation physics and chemistry. Although the fragmentation processes of various molecules have been extensively studied, most studies have focused on specific pathways, such as two- or three-body fragmentation, which can be analyzed from coincidence detection of the fragment ions. Analysis of the product ions from larger molecules becomes difficult because larger numbers of ions can be produced from a single molecule. Possible production of neutral fragments further complicates the situation. The overall picture of the fragmentation processes of multiply charged polyatomic molecules is thus still unclear. The electron counting technique developed by Martin et al.^[4] can be used to systematically investigate fragmentation of multiply ionized molecules in fast heavy ion collisions. Coincidence measurements of the number of emitted electrons provide information about the product ion species as functions of the degree of multiple ionization irrespective of the number of fragments, including neutral fragments. We have previously revealed the fragmentation patterns from the multiply ionized states of various polyatomic molecules.^[5–8]

Recently, we implemented a momentum imaging technique to systematically investigate the KE distributions (KEDs) of product ions as functions of the intermediate charge state. In a previous study, we demonstrated a measurement with an acetylene (C_2H_2) target.^[9] In this work, we extend the study to ethane (C_2H_6), which contains

more hydrogen atoms than acetylene. Examination of the KEDs with respect to the number of broken C–H bonds reveals the role of hydrogen emission in the fragmentation dynamics. In addition, H_3^+ emission was investigated as a characteristic product ion from multiply charged C_2H_6 .

2. Experimental method

The experiment was performed at the 1.7 MV tandem accelerator facility of the Quantum Science and Engineering Center, Kyoto University. The experimental procedure was essentially the same as in our previous study.^[9] Thus, only the relevant aspects will be outlined here. A well-collimated beam of 1.2 MeV C^{2+} was incident on the C_2H_6 gas target. To select the single electron capture collisions, the outgoing C^+ ions were separated from the other charge states (C^{q+} , $q \neq 1$) by an electrostatic deflector and selectively detected by a semiconductor detector (SSD_p). The signals from the SSD_p were used as the trigger of the following measurements. The electrons emitted in the collisions were detected by another semiconductor detector (SSD_e). The SSD_e was placed on a +25 kV high voltage stage to accelerate the electrons to the detectable energy of 25 keV. Pulse height analysis of the SSD_e signals provides information about the number of electrons emitted in each collision event n_e because the pulse height corresponds to $25n_e$ keV. In the single electron capture condition, the charge state of the intermediate $\text{C}_2\text{H}_6^{r+*}$ ion can be determined by $r = n_e + 1$. The product ions were extracted to a linear time-of-flight (TOF) mass spectrometer based on the velocity map imaging technique^[10] and detected by a multichannel plate (MCP) detector combined with a position-sensitive delay-line anode. Examples of the two-dimensional images of C_2H_6^+ , C_2^+ , CH_3^+ , and H^+ on the MCP detector are shown in Fig. 1. The distance from

the center position represents the KE of the product ion in the direction parallel to the detector plane. Intact C_2H_6^+ ions form a small spot because of negligibly small momentum transfer. The full width at half maximum of the C_2H_6^+ spot is less than 1.4 mm. The lighter fragment ions spread to larger regions because of their higher KEs received during fragmentation. The image of CH_3^+ has a structure with an outer ring and a central spot. This indicates that the KE distribution of CH_3^+ consists of two main components, which will be discussed in Section 3.2. The three-dimensional momentum of each product ion was obtained from the TOF and the position on the MCP detector. The ion signals were recorded together with the pulse height of the SSD_e signal event by event, which allows the fragmentation pattern^[5–8] and momentum of each product ion^[9] to be analyzed as a function of the charge state of the intermediate $\text{C}_2\text{H}_6^{r+*}$ ion.

3. Results and discussion

3.1. KEDs of C_2H_n^+ ($n = 0–6$)

The KEDs of the product ions of C_2H_n^+ for $n = 0–6$ produced by emission of neutral and ionized hydrogen species are plotted as “total” distributions in Fig. 2. The widths of the total distributions are substantially different for $n \geq 4$ and $n \leq 3$. The C_2H_n^+ ions for $n \geq 4$ have low KEs below 0.3 eV, while those for $n \leq 3$ spread up to about 1 eV. To understand the underlying causes, the contributions from the different charge states of the intermediate $\text{C}_2\text{H}_6^{r+*}$ ions are also plotted in the figures. They clearly show that the large broadening of the total KEDs for $n \leq 3$ is caused by the contributions of the multiply ionized states ($r \geq 2$).

C_2H_5^+ and C_2H_4^+ do not gain large KEs because they are almost exclusively produced from the singly charged intermediate ions ($r = 1$) through emission of neutral

hydrogen species. As mentioned in a previous paper,^[7] C_2H_5^+ and C_2H_4^+ are expected to be produced from singly charged $\text{C}_2\text{H}_6^{+*}$ excited states with low energy barriers according to the appearance energies of 11.46, 12.7, and 11.90 eV for production of C_2H_6^+ , $\text{C}_2\text{H}_5^+ + \text{H}$, and $\text{C}_2\text{H}_4^+ + \text{H}_2$, respectively.^[11] Comparing the KEDs of C_2H_n^+ for $r = 1$, the KED becomes broader with decreasing n . This shows that higher internal excitation is involved in emission of more neutral hydrogen.

C_2H_n^+ with $n \leq 3$ can gain larger KEs because of the contributions of the multiply charged intermediate states ($r \geq 2$) as significant production channels. Coulomb repulsion from the other fragment ions enhances the KEs of C_2H_n^+ . Moreover, the contributions from higher charge states ($r \geq 3$) increase with decreasing n . However, in this regard, the KEs for $r \geq 3$ do not further broaden even as r increases in contrast to the expectation from a higher Coulomb potential. Increase of fragment hydrogen ions does not enhance the KEs of C_2H_n^+ , probably because the Coulomb repulsive forces are somewhat canceled by the symmetric geometrical distribution of the hydrogen atoms. In a previous paper, a simpler example of reduction of the KE owing to symmetric fragmentation was reported for acetylene with the following pathway: $\text{C}_2\text{H}_2^{3+} \rightarrow \text{H}^+ + \text{C}_2^+ + \text{H}^+$.^[9]

3.2. KEDs of CH_n^+ ($n = 0-3$)

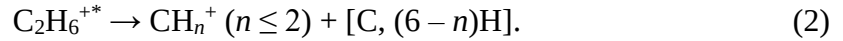
The KEDs of CH_n^+ for $n = 0-3$, which are produced through C–C bond breaking, are shown in Fig. 3. The total distributions extend up to about 6 eV. The shapes of the distributions are greatly different for different n . This can be attributed to variation of the distributions for specific r and their relative fractions depending on n . Note that the sharp peak at around 0 eV in the KED of CH_2^+ comes from $r = 2$. This component can

be ascribed to metastable $\text{C}_2\text{H}_4^{2+}$, rather than CH_2^+ , because the distribution is nearly equivalent to those of C_2H_n^+ for $n \geq 4$. In contrast, the KED of CH_3^+ for $r = 2$ has no strong peak at around 0 eV. This means that doubly charged intact $\text{C}_2\text{H}_6^{2+*}$ ions cannot survive during the TOF measurements. They dissociate because of the low energy barrier for H_2 emission and are stabilized by H_2 emission.

Unlike the KED of CH_2^+ , the low-energy peak at around 0 eV in the KED of CH_3^+ originates from $r = 1$. It has a peak at less than 0.5 eV. The KEDs of CH_2^+ , CH^+ , and C^+ for $r = 1$ have no sharp peak in this energy range and exhibit broad distributions up to about 3 eV. This indicates that the fragmentation pathway



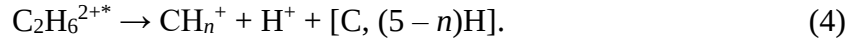
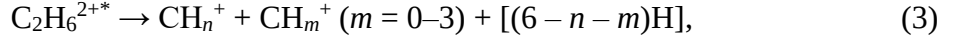
has a lower KE release (KER) originating from lower excited states compared with the pathways



Note that $[\text{C}, 3\text{H}]$ and $[\text{C}, (6 - n)\text{H}]$ just indicate the constituent atoms of the neutral fragments because their molecular compositions are unknown. These results are consistent with the KEDs reported in an electron impact experiment.^[12] At electron energies below the threshold of double ionization, the KE of CH_3^+ is distributed below 0.5 eV and the CH_2^+ ions have KEs ranging up to more than 1 eV. They agree well with the present results for $r = 1$. In addition, another component at around 2 eV starts to appear at electron energies higher than 30 eV. The present results elucidate that these high-energy components are contributions from doubly charged intermediate ions ($r = 2$).

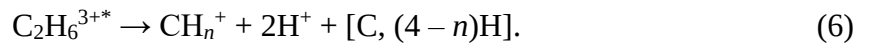
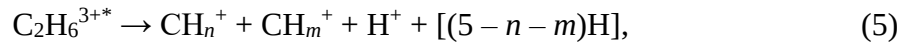
Except for the sharp peaks at around 0 eV, the large differences in the total KEDs are mainly because of the differences in the distributions for $r = 2$ and 3. In the KEDs of

CH^+ and C^+ , the peak at around 2.5 eV decreases with decreasing n and a lower energy peak appears at around 0.5 eV. To investigate the origin of the differences in the KEDs, the distributions at $r = 2$ are separately plotted in Fig. 3(e)–(h) for the following fragmentation pathways:



Fragmentation pathways (3) and (4) provide the peaks at the higher (~ 2.5 eV) and lower (~ 0.5 eV) energies, respectively. It is unsurprising that the KEs of CH_n^+ differ depending on the other simultaneously produced ion (CH_m^+ or H^+). They are qualitatively reasonable considering momentum conservation of the two fragment ions. The important point is that the predominant pathway shifts from (3) to (4) as n decreases. We found that CH_3^+ is rarely correlated with H^+ . With decreasing n , the probability of H^+ production is enhanced. As a result, CH_n^+ becomes preferentially correlated with H^+ . This example clearly demonstrates that multifragmentation caused by a high internal energy does not always lead to an increase in the KEs, as in the case of emission of C^+ fragment ions. It strongly depends on the fragmentation mechanism. In the present example, enhancement of C–H bond breaking leads to reduction of the KEs of CH_n^+ because H^+ removes a large fraction of the KER.

The same explanation applies to the KEDs for $r = 3$ with the following pathways:



The KEDs of CH_n^+ for $r = 3$ do not show a large increase in the KEs compared with $r = 2$. This means that additional H^+ emission does not greatly enhance the KEs of CH_n^+ . One reason is that CH_n^+ receive a small recoil from H^+ emission owing to the large

difference in mass between CH_n^+ and H^+ . In other words, most of the additional potential energy is removed by the fast H^+ emission. The other reason is the geometrical effect. The additional H^+ emission does not always act in the direction of the increase in the KE of CH_n^+ , as is the case with C_2H_n^+ discussed in Section 3.1. Following the above discussion, we expect that the KE of CH_n^+ does not greatly increase even for $r > 3$ unless a multiply charged C^{q+} fragment ion ($q \geq 2$) is produced.

3.3. KEDs of H_n^+ ($n = 1-3$)

The KEDs of H_n^+ for $n = 1-3$ are shown in Fig. 4. All of the total KEDs have a peak at around 4 eV. The peak positions are consistent with the results reported by infrared femtosecond laser irradiation, where the KEs of H^+ , H_2^+ , and H_3^+ produced in two-body fragmentation of C_2H_6 are 3.5, 3.5, and 3.6 eV, respectively.^[13] The peak width of the H^+ distribution is much broader than those of H_3^+ and H_2^+ . As previously reported,^[7] H_3^+ is predominantly produced from the doubly charged $\text{C}_2\text{H}_6^{2+*}$ ion. The distribution is narrower than the KED of H^+ for $r = 2$, indicating that H_3^+ is produced through excited states in a specific energy range. A small fraction of the H_3^+ ions are produced from $r = 3$. The small change of the mean KEs from $r = 2$ indicates a sequential fragmentation mechanism following prompt H^+ emission. Similar behavior is observed in the KEDs of H_2^+ .

In contrast to H_3^+ and H_2^+ , H^+ ions are generated from a wide range of charge states. To compare the structures of the KEDs at different r , the distributions normalized by each maximum intensity are plotted in Fig. 4(d). The peak positions greatly shift from $r = 1$ to 2, and the distribution becomes broader and extends to a higher KE with increasing r . It is reasonable for the KEDs of H^+ to directly reflect an increase in the

Coulomb potential because other fragments do not interfere with prompt H^+ ejection.

4. Summary

We have performed KED measurements of the fragment ions generated from multiply ionized C_2H_6 ions in single electron capture collisions with 1.2 MeV C^{2+} . The KEDs were systematically obtained as functions of the charge state of the intermediate ions $\text{C}_2\text{H}_6^{r+*}$ ions r by performing a coincidence measurement of the number of emitted electrons. The KEDs show that the substantial differences of the total KEDs of C_2H_n^+ for $n = 3$ and 4 are because of the contributions of the multiply charged intermediate states ($r \geq 2$). We found that the differences in the KEDs of CH_n^+ for different n can be attributed to the different preferential fragmentation pathways. In particular, an increase in H^+ emission leads to reduction of the KEs of CH_n^+ . In addition, the narrower KEDs of H_3^+ and H_2^+ compared with that of H^+ are probably because they are produced through specific excited states. In contrast to the other fragment ions, the KEs of H^+ are found to increase as functions of r in a straightforward manner.

Acknowledgments

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List of references

- [1] D. Mathur, *Phys. Rep.* **2004**, 391, 1.
- [2] L. Adoui et al., *Nucl. Instr. Meth. Phys. Res. B* **2006**, 245, 94.
- [3] T. Yatsushashi, N. Nakashima, J. Photochem. Photobiol. C **2018**, 34, 52.
- [4] S. Martin, L. Chen, A. Denis, J. Désesquelles, *Phys. Rev. A* **1998** 57, 4518.
- [5] T. Majima Y. Nakai H. Tsuchida, A. Itoh, *Phys. Rev. A* **2004**, 69, 031202(R).
- [6] T. Majima, Y. Nakai, T. Mizuno, H. Tsuchida, A. Itoh, *Phys. Rev. A* **2006**, 74, 033201.
- [7] T. Majima, T. Murai, T. Kishimoto, Y. Adachi, S. O. Yoshida, H. Tsuchida, A. Itoh, *Phys. Rev. A* **2014**, 90, 062711.
- [8] T. Majima, T. Murai, S. Yoshida, M. Saito, H. Tsuchida, A. Itoh, *Int. J. Mass Spectrom.* **2017**, 421, 25.
- [9] S. Yoshida, T. Majima, T. Asai, M. Matsubara, H. Tsuchida, M. Saito, A. Itoh, *Nucl. Instr. Meth. Phys. Res. B* **2017**, 408, 203.
- [10] D. H. Parker, A. T. J. B. Eppink, *J. Chem. Phys.* **1997**, 107, 7.
- [11] E. Vašeková, M. Stano, Š. Matejíček, J. D. Skalný, P. Mach, J. Urban, and T. D. Märk, *Int. J. Mass Spectrom.* **2004**, 235, 155.
- [12] C. Tian, C. R. Vidal, *J. Chem. Phys.* **1998**, 109, 1704.
- [13] K. Hoshina, H. Kawamura, M. Tsuge, M. Tamiya, M. Ishiguro *J. Chem. Phys.* **2011**, 134, 064324.

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Figure 1. Two-dimensional images of the (a) C_2H_6^+ , (b) C_2^+ , (c) CH_3^+ , and (d) H^+ product ions on the MCP detector. The projections onto the x and y axes are plotted for C_2H_6^+ .

Figure 2. (a)–(g) KEDs of C_2H_n^+ ($n = 0–6$) and the contributions of the specific charge states of the intermediate $\text{C}_2\text{H}_6^{r+*}$ ion ($r = 1–4$).

Figure 3. (a)–(d) KEDs of CH_n^+ ($n = 0–3$) and the contributions of the specific charge states of the intermediate $\text{C}_2\text{H}_6^{r+*}$ ion ($r = 1–4$). Note that (b) includes $\text{C}_2\text{H}_4^{2+}$. (e)–(h): KEDs for $r = 2$ separated by the two fragmentation pathways $\text{CH}_n^+ + \text{CH}_m^+$ and $\text{CH}_n^+ + \text{H}^+$.

Figure 4. (a)–(c) KEDs of H_n^+ ($n = 0–3$) and the contributions of the specific charge states of the intermediate $\text{C}_2\text{H}_6^{r+*}$ ion ($r = 1–4$). (d) Distributions of H^+ for $r = 1–4$ normalized by each maximum intensity.

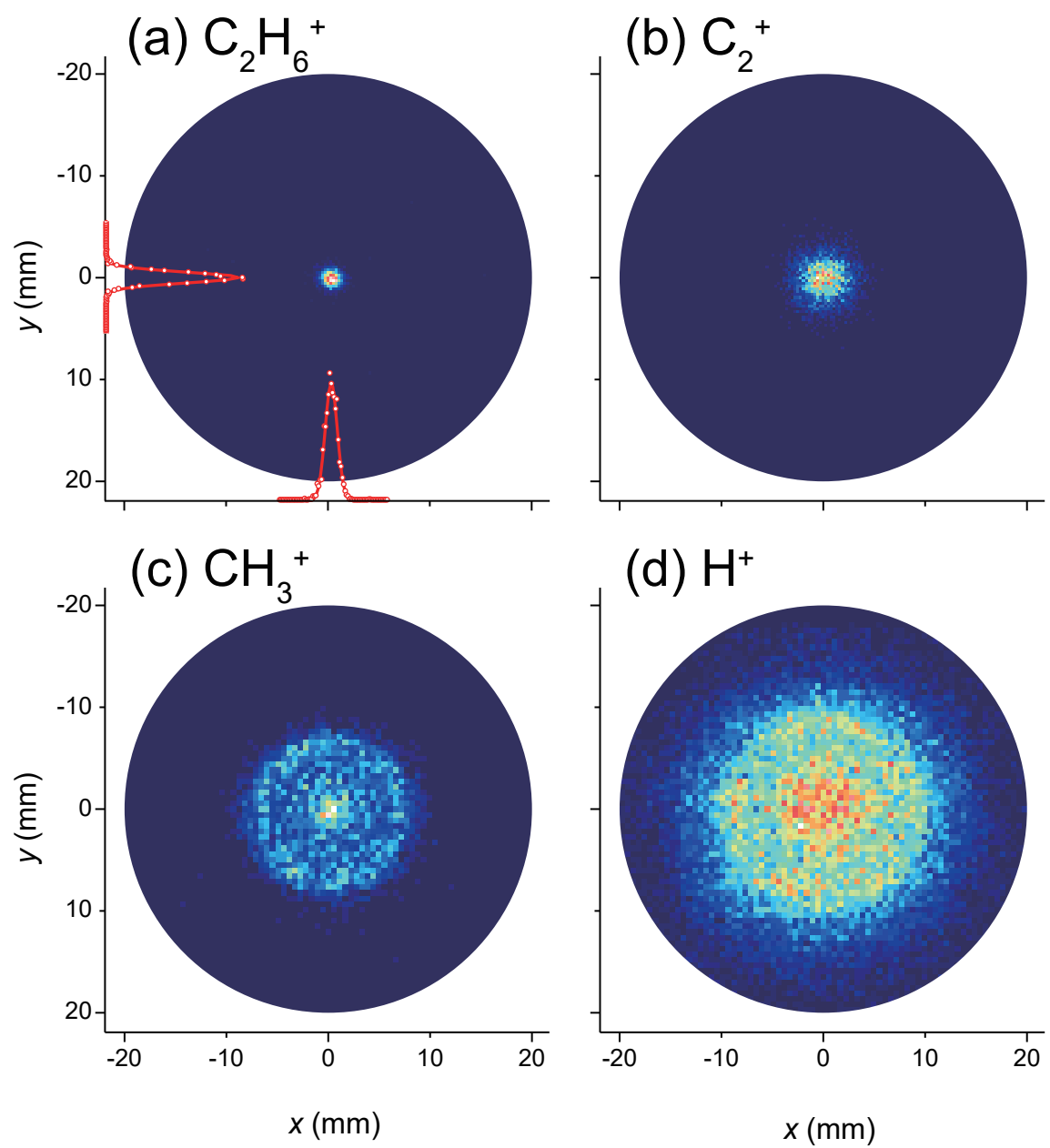


Fig.1

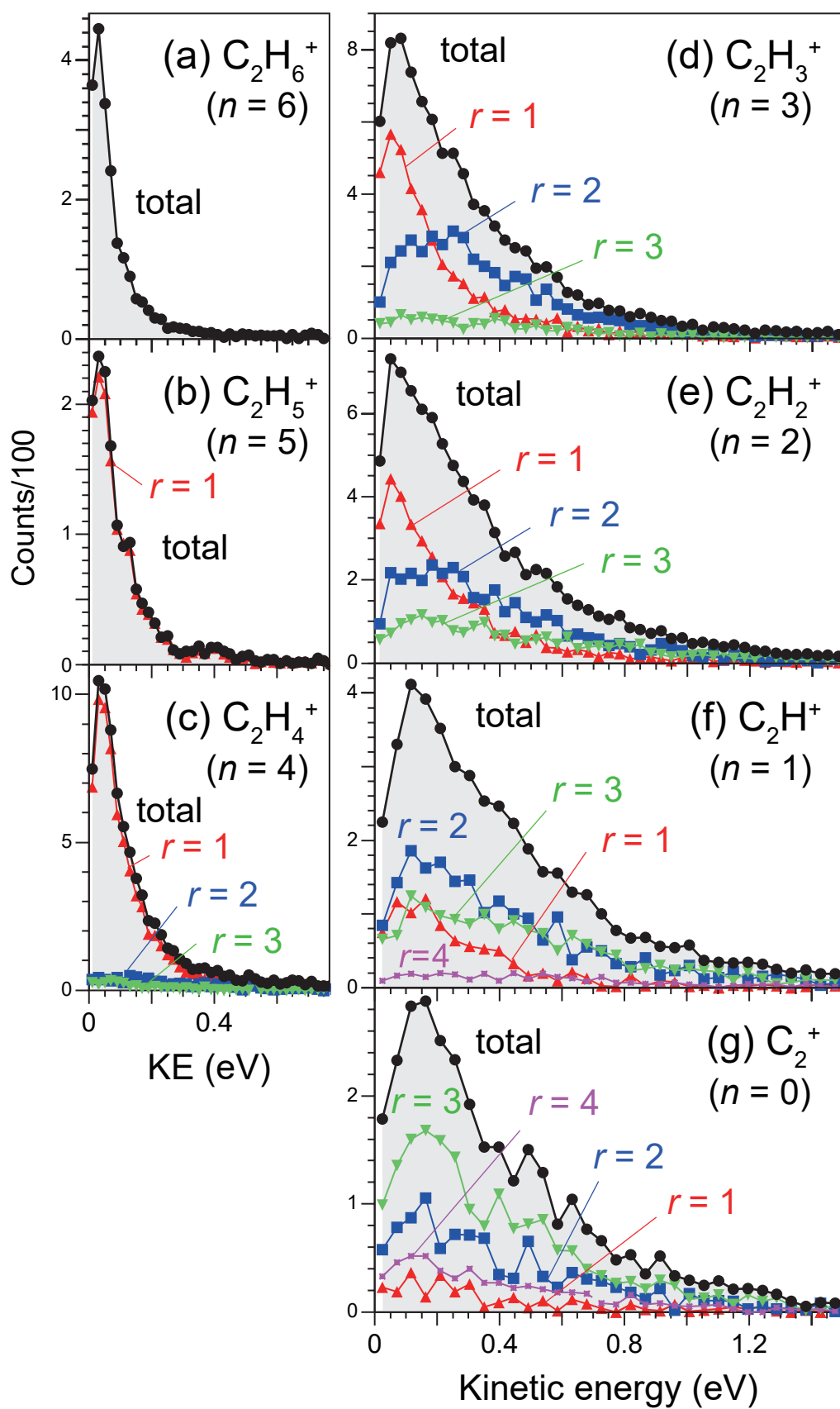


Fig.2

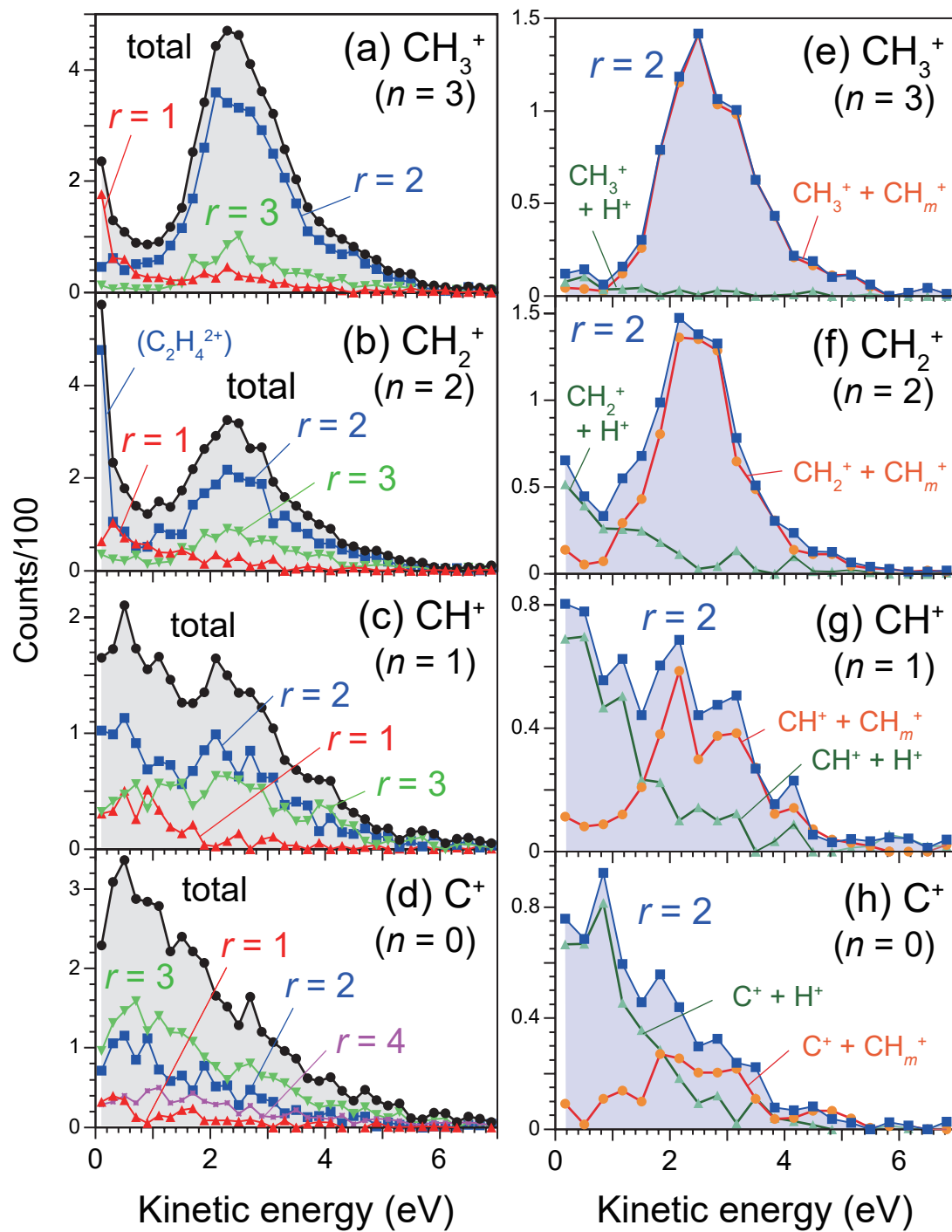


Fig.3

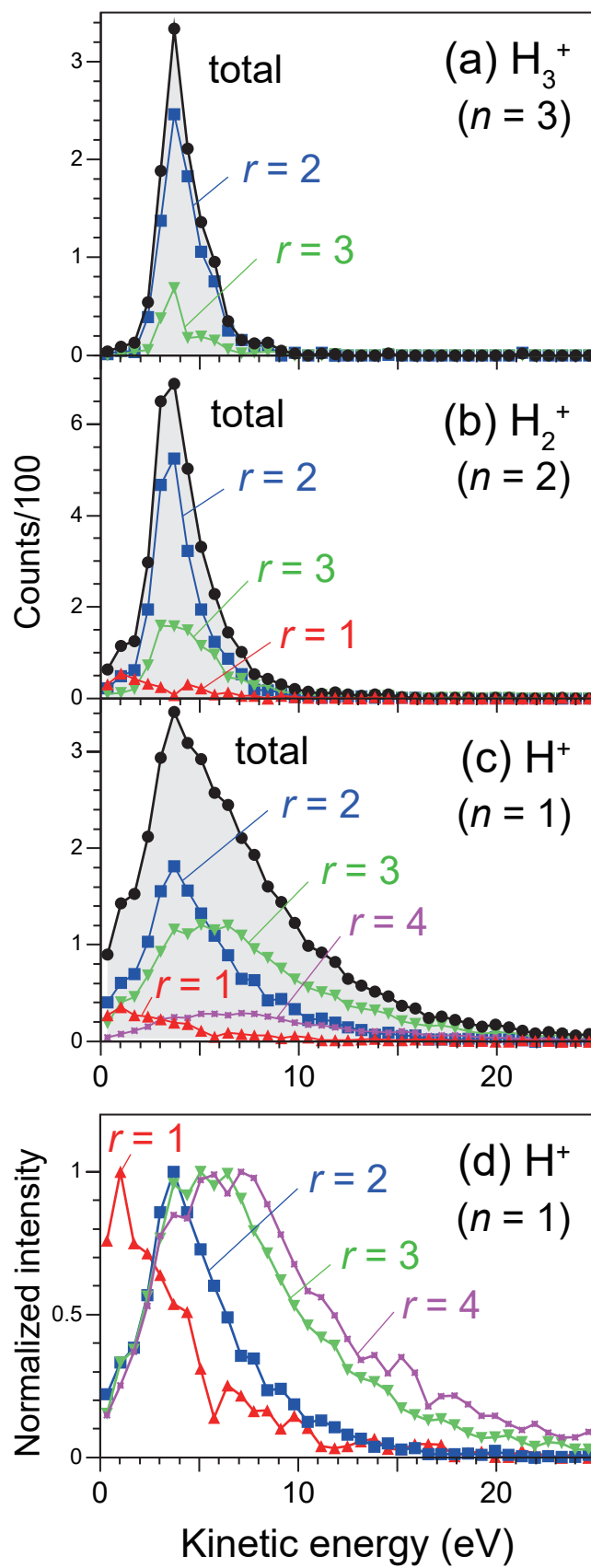


Fig.4