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DISSOCIATIVE NEUTRALIZATION OF H_2^+ AND HD^+ IONS BY ELECTRON TRANSFER FROM ALKALI METALS USING A NEGATIVE ION DETECTION METHOD

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主論文 2部

RELATIVE CROSS SECTIONS AND KINETIC ENERGY RELEASE VALUES IN DIS-
SOCIATIVE NEGATIVE ION FORMATION BY TWO ELECTRON TRANSFER FROM
ALKALI METAL TARGETS.

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ABSTRACT

Positive ions formed from C_2H_2 were collided with Cs, K, Na tar-
gets in the keV energy range. The dissociative negative ion for-
mations of C_2^- and C_2H^- ions from $C_2H_2^+$ ions and C_2^- ions from
C_2H^+ ions were determined to be two collision process with alkali
metal target using the target density dependence. Considering
the reaction energies and comparing with the reionization to
positive ions, main processes of the dissociative negative ion
formations were assigned to the successive single electron
transfers with the dissociations of excited neutrals. The
kinetic energy release (KER) values at FWHM of C_2H^- ions from
$C_2H_2^+$ ions were 0.55 eV for Cs, 0.28 eV for K and 0.17 eV for Na.
The relative cross sections of C_2^- ions from $C_2H_2^+$ ions to that
of C_2H^- ions from $C_2H_2^+$ ions were 5.35 for Cs, 1.89 for K and
0.32 for Na. These dependences on target species are discussed

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in the relation to the energy difference for the exothermic
neutralization.

INTRODUCTION

There have been many results reported on the dissociation of
ions over the past years.[1]   For the dissociation of neutral
species, in spite of its importance, much less work has been
reported than that for ions, owing to the difficulty of identi-
fication of neutral species by mass analysis.   Recently though,
some work has been reported using new techniques[2-9].   For
example, the Porter group[2-5] has detected energetic neutrals by
a magnetic electron multiplier which was translated perpendicular
to the beam axis.   de Bruijn et al.[6,7] and Körnig et al.[9]
used the coincidence method for time difference and position dif-
ference to detect the dissociated neutral species.   This method
has the advantage of being able to measure the dissociation to
two fragments very precisely, but is unable to detect dissocia-
tion in which mass ratios of dissociative fragments are smaller
than 6.2, as pointed out by Körnig.

On the other hand, the importance of the neutralization re-
ionization method to mass analysis was pointed by McLafferty,
[10,11] Schwarz[12,13] and Holmes[14].   The possibility of
differentiating among isomeric ions of hydrocarbons was reported
by the McLafferty group [15,16] using the neutralization reioni-
zation to positive and negative ions.   Burgers et al.[17] also
reported the same possibility with some organic compounds by
using the alkali metal vapor.   Wesdemiotis and Feng[18] measured

the neutralization reionization efficiencies for $C_3H_n^+$ ions (n = 0 to 6) to positive ions and negative ions, where the reionization gases were O_2 and Xe, respectively. Hudgins et al.[19] researched the neutralization of $C_2H_2^+$ and $C_2H_3^+$ ions on metal targets using both the neutral detection method and the neutralization reionization method by NO_2 charge stripping. In this work, by measuring the dissociative negative ion formation from the positive ions which were obtained from C_2H_2, neutralizations of $C_2H_2^+$ and C_2H^+ ions involving loss of H atoms have been investigated. These data yielded the complementary information for the neutralization of $C_2H_2^+$ ions to the reionization to positive ions by Hudgins et al.[19]

EXPERIMENTAL

The experimental apparatus and the procedure were essentially the same as that used previously.[8,20] Figure 1 shows a detailed schematic of an ion source (IS) and a target chamber (TCH). The TCH made of copper was developed to improve the uniformity and stability of the temperature. The gold plates were used as the slits of the TCH. The experimental procedure will only be reviewed shortly here. The positive ions were produced by the 100 eV electron impact to C_2H_2 gas from F_{IS}. These ions were accelerated by the potential difference between the IS and

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the TCH and entered the TCH without mass analysis. The 50 mm long TCH was located about 25 mm apart from the IS. The negative ions produced by two electron transfer in the TCH were mass-analyzed by a 90° magnetic sector with a 200 mm ion orbital radius. The alkali metal vapor was supplied from the reservoir which contained alkali metals by heating it. The purity of each alkali metal was measured from mass analysis of the positive ions produced by electron impact from F_{TCH}. The negative ion spectra in this work were measured under the condition of more than 99% purity of respective alkali metals. The relative density of the alkali metal vapor in the TCH was measured using the alkali metal effused from a hole on the TCH by a surface ionization type monitor. The absolute density of alkali metal was estimated from the temperatures of the reservoir and the TCH. The intensities of incident positive ions were measured by reversing the polarity of the magnet.

RESULTS AND DISCUSSION

The negative ion spectra with a Cs target at the collision energy of 3.0 keV are shown in Fig.2. The relative intensity of incident positive ions entering the TCH was 100 / 23 / 7.8 for $C_2H_2^+$ / C_2H^+ / C_2^+. The apparent masses of the peak top for a, b, d and e were 22.1, 23.3, 24.0 and 25.0, respectively. These

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peaks were assigned as C_2^- ions from $C_2H_2^+$ ions for the peak a, C_2^- ions from C_2H^+ ions for the peak b, non-dissociative C_2^- ions for the peak d and non-dissociative C_2H^- ions for the peak e. The estimated apparent mass for C_2H^- ions from $C_2H_2^+$ ions was 24.04, and therefore this peak, denoted as the peak c, was overlapped with non-dissociative C_2^- ions. These assignments were confirmed by the peak shifts with different voltages of the IS and the TCH. The dissociative peaks a, b and c were broad because of the kinetic energy releases from dissociation, while the peaks of non-dissociative C_2^- ions (d) and C_2H^- ions (e) were sharp. Target density dependence for non-dissociative peaks was different from that for dissociative peaks as shown in the spectra with the different densities. The density dependences of dissociative peaks were identical to each other.

To examine the target density dependence precisely, the changes of the negative ion intensity and the alkali metal density in the TCH were measured simultaneously. The supply of alkali metal vapor from the reservoir to TCH was decreased by cutting off the heat to the reservoir. The negative ion intensity is plotted against the monitor current in Fig.3. C_2^- ions from $C_2H_2^+$ ions and He^- ions from He^+ ions were measured under the condition that the voltages of the IS and the TCH were 3.0kV and 0.0 kV, respectively. For non-dissociative C_2H^- ions, in order to avoid interference from overlapping with the isotope peak of peak c, the voltage of IS = 0.5 kV and that of TCH = -1.25 kV
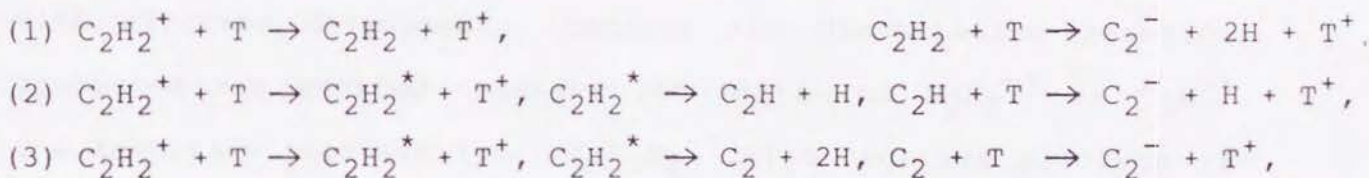
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were selected. Non-dissociative peaks which showed the linear dependence on the target density were discussed in the previous paper[20]. Non-dissociative successive single electron transfers for both C_2H^- and C_2^-, which are predicted to show the square dependence on target density, were not observed. Identically to He^- ions from He^+ ions, C_2^- ions from $C_2H_2^+$ ions showed the square dependence on the target density. Because He^- ion formation has been reported to be the successive single electron transfer[21], it was concluded that these dissociative processes were two collision processes with alkali metal targets. The other dissociative processes are also deduced to result from the two collision processes, from the agreement of the peak ratios in the different target densities as shown in Fig.2.

The changes in the negative ion mass spectra produced by different target species are shown in Fig.4. Non-dissociative C_2^- and C_2H^- ion peaks were not detected for the Na and K targets. A small broad peak observed near $m/z = 25$ for the K and Na targets was explained as the isotope peak of the peak c. The dissociative peaks of a,b and c observed with Cs target are also observed with the K and Na targets. The relative intensities of these peaks showed a large dependence on the target species. The peak width also changed for different targets. The width of the peak for C_2^- ions from $C_2H_2^+$ ions for Na target is slightly narrower than that for K and Cs target in Fig.4. These dissociative peaks were also confirmed as resulting from the two
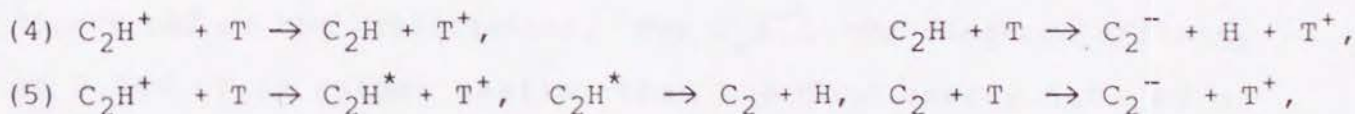
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collision processes with alkali metals using the target density dependences.

The reaction mechanism of dissociative a,b and c peaks were assigned using the reaction energies and the comparison of this data with the neutralization reionization data by Hudgins et al. Ionization potentials (IP), electron affinities (EA) and bond energies (BE) are tabulated in Table 1, where ionization potentials were derived from references[22,23], electron affinities were evaluated from photoelectron measurement[24] and bond energies were calculated from references[25,26]. The reaction mechanisms which have the possibility of explaining dissociative peaks formed from two collision processes are as follows, where T is a target,
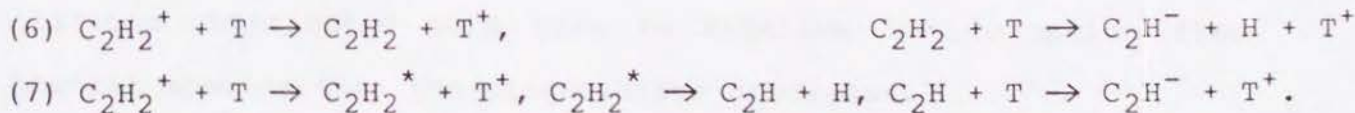
for peak a;

(1) $C_2H_2^+ + T \rightarrow C_2H_2 + T^+$, $\qquad C_2H_2 + T \rightarrow C_2^- + 2H + T^+$.

(2) $C_2H_2^+ + T \rightarrow C_2H_2^* + T^+$, $C_2H_2^* \rightarrow C_2H + H$, $C_2H + T \rightarrow C_2^- + H + T^+$,

(3) $C_2H_2^+ + T \rightarrow C_2H_2^* + T^+$, $C_2H_2^* \rightarrow C_2 + 2H$, $C_2 + T \rightarrow C_2^- + T^+$,

for peak b;

(4) $C_2H^+ + T \rightarrow C_2H + T^+$, $\qquad C_2H + T \rightarrow C_2^- + H + T^+$,

(5) $C_2H^+ + T \rightarrow C_2H^* + T^+$, $C_2H^* \rightarrow C_2 + H$, $C_2 + T \rightarrow C_2^- + T^+$,

for peak c;

(6) $C_2H_2^+ + T \rightarrow C_2H_2 + T^+$, $\qquad C_2H_2 + T \rightarrow C_2H^- + H + T^+$

(7) $C_2H_2^+ + T \rightarrow C_2H_2^* + T^+$, $C_2H_2^* \rightarrow C_2H + H$, $C_2H + T \rightarrow C_2H^- + T^+$.

The reactions (1), (4) and (6) consist of non-dissociative neutralizations and dissociative anionizations, while the reactions

(3), (5) and (7) consist of dissociative neutralizations and non-dissociative anionizations. The reaction (2) is composed of a dissociative neutralization and a dissociative anionization. The reaction energies for each processes were evaluated from the values in Table 1 and are shown in Table 2.

The above dissociative anionizations have much larger endo-thermicities than non-dissociative processes, as shown in Table 2. "Adiabatic criterion"[27], in which a value of an adiabatic parameter was given as 7Å, theoretically predicted that about 1 eV endothermicities would give the largest cross section for electron transfer in keV order collisions with regard to the 20 to 30 mass units ions. Therefore the non-dissociative processes were expected to contribute mainly to negative ion formations. Moreover the dissociation to produce negative ions had to compete with electron detachments, because the dissociative reactions proceeded via excited negative ion states of $C_2H_2^{-*}$ or C_2H^{-*}. The temporary negative ions of $C_2H_2^{-*}$ with negative electron affinity would be predicted to detach an electron with high efficiency before the dissociation. For C_2H^{-*}, the electron affinity of 2.969 eV is rather smaller than the bond energy 5.03 eV of $(C_2-H)^-$. It would be concluded that the non-dissociative anionizations contributed much more to negative ion formation from neutral species than the dissociative processes.

Using the reionization method with the charge stripping gas of NO_2 for the neutralization of $C_2H_2^+$ ions with alkali metals,

Hudgins et al. [19] reported that the relative reionized intensities of $C_2H_2^+$ / C_2H^+ / C_2^+ were -/55/45 for K target and 7/60/33 for Na target. In their work, an ion beam was produced by either chemical ionization (CI) or electron impact (EI) in a higher pressure source which was different from low pressure EI in my work. $C_2H_2^-$ ions were not observed in my work because of the negative electron affinity of C_2H_2. Relative ion intensities of C_2H^- / C_2^- were 35 / 65 for K target and 76 / 24 for Na target. The relative intensities of C_2H / C_2 in the reionization to both positive and negative ions decreased with the ionization energies of targets in the neutralization. The lack of $C_2H_2^+$ ions in the reionization to the positive ions for K target by Hudgins et al.[19] indicated that most excited $C_2H_2^*$ formed from exothermic neutralization dissociated into C_2H and/or C_2. For Cs target with smaller ionization energy than K target, neutralized $C_2H_2^*$ would dissociate more perfectly. From this result and the above mentioned discussions on the endothermicities in the anionizations, C_2H^- formation from $C_2H_2^+$ ions (peak c) was assigned to the reaction (7), not to the reaction (6). As a result of this assignment for peak c, the non-dissociative anionization for C_2H^- ions was found to have sufficient cross section to detect negative ions as predicted by "adiabatic criterion".[27]

The lack of non-dissociative successive single electron transfer of C_2H^- ions from C_2H^+ ions in this work indicated that

most of the neutralized C_2H^* dissociated, since the non-dissociative C_2H^- ion formation from C_2H had a sufficient cross section to detect negative ions. The dissociation of most of the C_2H^* coincided with that of $C_2H_2^*$ because the neutralization of C_2H^+ had larger exothermicity than that of $C_2H_2^+$. Therefore the C_2^- formation from C_2H^+ ions (peak b) was assigned to the reaction (5), not the reaction (4). The non-dissociative negative ion formation of C_2^- would also have sufficient cross section to detect negative ions.

Dissociative neutralizations of cyclohexane ions for alkali metal targets in which two C-C bonds had to cleavage were confirmed by a neutral detection method [9]. The neutralizations were more than a few eV endothermic. In dissociative neutralization measured by de Bruijn et al.[6], more than a few eV endothermic processes with large KER values of about 8 eV with Ar, Mg, Na and Cs targets were also observed with sufficient intensities. KER values for dissociative negative ion formations of H_2^+ and HD^+ ions with alkali metal targets in our laboratory showed the good agreement with the dissociative neutralization. By this agreement the H^- and D^- ion formations with the large KER values has been assigned to few eV endothermic neutralization and endothermic anionization. Considering the endothermicities for neutralization and the cross sections of anionizations, the reaction (3) would be the main process for C_2^- ion formation from $C_2H_2^+$ ions (peak a) because the non-

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dissociative C_2^- ion formation had sufficient cross section, though the process (2) could not be perfectly denied.

There is no contradiction between this explanation for the dissociative C_2^- ion formation from $C_2H_2^+$ ions and that for the C_2^+ ion formation by Hudgins et al.[19]. For only positive ion formations, they claimed that neutralized $C_2H_2^+$ yielded predominantly C_2H + H and that C_2^+ was due to dissociative reionization of C_2H. While the dissociative process from C_2H_2 to C_2H in the positive ion formation was the same as that in the negative ion formation, the dissociative process from C_2H_2 to C_2 in positive ion formation was different from that in the negative ion formation in which $C_2H_2^+$ dissociated into C_2 in endothermic neutralization. The difference in intensity ratios of C_2/C_2H between positive and negative ion formation from C_2H_2 would be attributed to the difference in C_2 formation processes, though an influence of the difference in ionization method between CI and EI could not be ignored. By these considerations the dissociative two electron transfers were explained by the successive single electron transfer with the dissociation. It was now concluded that the dissociation mechanism would proceed via excited neutrals formed from the exothermic neutralizations. These mechanism were consistent with the dependences of relative cross sections and KER values on target species, as described below.

The kinetic energy release (KER) values for the full width at

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half maximum (FWHM) of the peaks were evaluated using an equation reported in another paper[28] and are shown in Table 3. Though there is an apparent discrepancy of KER values for K target between 0.28 ± 0.03 eV for C_2H^- ion formation and 1.3 ± 0.2 and 1.4 ± 0.2 eV for C_2H formation from $C_2H_2^+$ ions by Hudgins et al.[19], the experimental data of the reionization to negative ions do not contradict that of the reionization to positive ions. Hudgins et al. measured only the maximum scattering angle corresponding to the highest fragment kinetic energy released for C_2H formation from $C_2H_2^+$ ions. In my work the average kinetic energy release were evaluated from the full width at half maximum (FWHM). The maximum beam spread in the neutral beam profile would be corresponding to a full width at ten maximum (FWTM) of dissociative peak in the negative ion spectra. The KER value evaluated from FWTM was 1.2 ± 0.1 eV, which showed considerable agreement with that by Hudgins et al.[19] The agreement supported the presumption that the dissociation of H atoms in dissociative C_2H^- ion formation from $C_2H_2^+$ happened in exothermic neutralization. The agreement in different ionization method for a primary beam between EI and CI would show that almost of $C_2H_2^+$ ions which were formed by EI and dissociated to $C_2H + H$ in the neutralization were not highly excited.

The equation to evaluate the KER values is valid for dissociation into two fragments. The KER values for C_2^- ions from $C_2H_2^+$ ions in Table 3 were evaluated using the assumption

that $C_2H_2^*$ dissociated into two fragments of C_2 and H_2. Actually, this assumption could not be valid, because the two H atoms are on opposite sides of the C-C bond. If $C_2H_2^*$ dissociates one H atom, the KER values for this process become about twice the values shown in Table 3. If the excited $C_2H_2^*$ dissociates two H atoms with almost the same energy at opposite sides simultaneously, the kinetic energy releases would counteract each other and the KER values would become much smaller than the values shown in Table 3. These considerations suggest that H atom dissociations occur as the two stage process. The time difference between two stages is smaller than 3.3 ns because the second electron transfer to produce negative ions after the dissociations had to occur in TCH.

In all reactions, the KER values shown in Table 3 decreased with increase of the ionization potential of the target. This result indicates that with the ionization potential of the targets becoming lower, the product neutrals were excited into the higher level. The KER values of peak b and c in the exothermic neutralization of the reactions (5) and (7) have a parallel relation to the exothermicities, regardless of the target species and the reactions. The reactions (5) and (7) which involve dissociation of one H atom have exothermicities of a few eV which were larger than the KER values. This indicates that some of exothermic energies are stored in vibrational and/or rotational modes of the neutral product. As seen in Table 3, the

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ratios of the KER values of peak b and c to the exothermicities for the reaction (5) were larger than those for the reaction (7) in any target species. This result shows that the existence of more vibrational mode would contribute to store the more internal energy, because C_2H has more vibrational modes than C_2. The KER values of peak a for the endothermic reactions (3) were comparable to those for exothermic reactions (5) and (7). This indicates that some of the collision energy was transferred into the internal energy of neutral product in the collisions. If the translation from the collision energy to internal energy is taken into account in the case of the exothermic reaction as well, higher excited level than expected from exothermicity may exist in the exothermic reactions (5) and (7).

Relative cross sections at the collision energy of 3.0 keV are shown in Table 4. The dependences for both relative cross sections on the target species can be explained by that near resonance gives a large cross section. The exothermicities of the neutralization are illustrated in Fig.5. Both relative cross sections (a)/(b) and (a)/(c), decreased with increase of the ionization potential of the target. The relative cross section for the reaction (a)/(b) showed a small decrease from Cs to Na. Since the negative ion formation is the same process for the reactions (3) and (5), the dependence on the target species for the relative cross section (a)/(b) is due to neutralizations. In the variation from Cs to Na C_2H formation from $C_2H_2^+$ ions in the

reaction (7) became closer to resonance than C_2 formation from C_2H^+ ions in the reaction (5). The small decrease of the relative cross section (a)/(b) from Cs to Na were explained by the decrease of the exothermicities of the neutralization. By contrast, the relative cross section for the reaction (a)/(c) showed a large decrease of 16th times from Cs to Na. The endothermicities of non-dissociative anionizations for C_2H^- ions were 0.30 eV larger than that for C_2^- ions in any target as shown in Table 2. Though this difference is one of factors which determined the cross section, this small difference would not explain the large dependence on target species between C_2H^- and C_2^- ion formation from $C_2H_2^+$ ions. The endothermicity for the reaction (3) becomes larger from Cs to Na, while the exothermicity for the reaction (7) becomes smaller from Cs to Na. Therefore the dependence of the relative cross section (a)/(c) on the target species would be mainly due to the neutralizations.

The vibrational excitations to dissociate one or two H atoms are considered to be caused by the energy relaxation from the electronic excited molecules which are formed by the near resonance neutralization. To dissociate H atoms excitations in vibrational mode between C and H should be higher than the dissociation limit. If the highly vibrational excitation occur directly in the electron transfer collisions, hard collisions with small impact parameters should occur. The product of absolute cross sections of neutralization and negative ion

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formation for C_2H^- formation from $C_2H_2^+$ ions with Na targets was estimated tentatively as 1.3×10^{-30} cm^4. This value is much larger than that of the product of ordinary collision processes of $\sim 10^{-16}$ cm^2. Provided that the cross section of the endothermic negative ion formation was 10^{-16} cm^2, the cross section for the neutralization is derived as about 10^{-14} cm^2. This large value shows the good agreement with those reported for the neutralization of the H_3O^+, NH_4^+ and CH_5^+ ions with K and Na targets [3]. These large cross sections show that the neutralization proceeds via near resonant processes with large impact parameters. The electronic excited molecules formed via near resonance processes relax the electronic energy to vibrational modes and dissociate H atoms.

The electronic states of the molecules formed from the electron transfer was presumed using the excitation energy and the geometry change between the primary ions and formed molecules. The ground state of $C_2H_2^+$ ion is $^2\Pi_u$ with the linear geometry belonging $D_{\infty h}$ point group[29]. The excitation levels of singlet states for C_2H_2 were compiled by Herzberg[30]. The low lying singlet $\tilde{A}^1A_u$ state is 5.2 eV higher than the ground state has the bend geometry belonging C_{2h}. Robert et al. reported the onset of the second low lying $\tilde{B}^1B_u$ state as 6.68 eV using the photoabsorption spectra.[31]. The $\tilde{A}^1A_u$ state is lower than the dissociation limit of $C_2H + H$, while the $\tilde{B}^1B_u$ state is higher than that. Energy levels of $\tilde{a}$ and $\tilde{b}$ triplet states were

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reported at 5.2 and 6.1 eV from the ground state by Trajmar et al.[32], respectively. The geometry of $\tilde{b}^3\Delta_u$ state were calculated as linear by Kammer[33]. The formation of both the singlet and the triplet states of C_2H_2 by one electron from alkali metal conserves total spin of the system. When the excitation of $C_2H_2^+$ into the $\tilde{b}^3\Delta_u$ state occurs for the Na target, the exothermicity is 0.16 eV, indicating that this process is the nearest resonant among these states. The dependence of the relative cross sections for reaction (a)/(c) on the target species is explained by the process to form the $\tilde{b}^3\Delta_u$ state of excited $C_2H_2^*$ which would be most probable to dissociate to C_2H + H in high efficiency. Some higher states such as the $\tilde{B}$ state, the $\tilde{C}$ state and the $\tilde{D}$ state with the linear geometry may also be involved in the dissociation mechanism to form C_2H + H. The highest state reported for C_2H_2 by Herzberg [30] is $\tilde{G}^1\Pi_u$ state which is lower than the dissociation limit of C_2 + 2H. High Rydberg states may be involved in the dissociation to C_2 + 2H.

The electronic states of the excited neutral from C_2H^+ ions could not be presumed. To our knowledge, the higher electronic excited level of C_2H has not been reported, except by Okabe[34] who reported the energy level as 4.11 eV higher than the ground state. This state is a few eV lower than the dissociation limit of C_2 + H. Therefore this implies the involvement of other higher electronic excitation states of the C_2H radicals.

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Figure Caption

Fig.1.   Schematic of an ion source and a target chamber. F_{IS}
and F_{TCH} are filaments for electron impact attached to the IS and
TCH, respectively. Both L1 and L2 are half plate lenses.   The
voltages of IS and TCH could be changed independently of each
other.   Alkali metal targets are supplied as vapor from a
reservoir.   A monitor is a surface ionization type and measure
alkali metals effused from a hole on the TCH.

Fig.2.   Negative ion spectra measured with a Cs target and the
collision energy of 3.0 keV at different target densities from
$m/z = 20$ to $m/z = 26$. The spectra were normalized with respect to
the most intense peak.   The density ratio was 1 (Low) : 2.2
(Middle) : 5.3 (High). The peak near $m/z = 24$ was overlapped by
the nondissociative C_2^- ions (d) and C_2H^- ions from $C_2H_2^+$ ions
(c).

Fig.3.   Target pressure dependence of the some product negative
ion intensities.   The proportionality between the monitor
current and the target density was confirmed by measuring the
dependence of the monitor current on the temperature of the

reservoir by maintaining the TCH at constant temperature. $\bigcirc$: He^- ions from He^+ ions, $\triangle$: C_2^- ions from $C_2H_2^+$ ions and $\square$: C_2H^- ions from C_2H^+ ions. Slopes of the lines calculated by a least square method for He^- from He^+, C_2^- from $C_2H_2^+$ and C_2^- from C_2^+ were 1.84, 1.73 and 0.91, respectively. Discrepancies from the integral number of 2, 2 and 1 were mainly due to a back ground current in the monitor current. Comparing with He^- ion formation which shows square dependence has been reported as a successive single electron transfer[12], main target dependences of C_2^- from C_2H_2 and C_2^- from C_2^+ could be determined as 2 and 1, respectively. While non-dissociative C_2H^- ions show linear dependence, dissociative C_2^- ions show square dependence.

Fig.4. Dependence of the negative ion spectra on the target species. While the peak of C_2^- ions from $C_2H_2^+$ ions, a, is the main peak for the Cs and K target, that of C_2H^- ions from $C_2H_2^+$ ions, c, is the main peak for the Na target. The peak widths become narrower from the Cs target to the Na target.

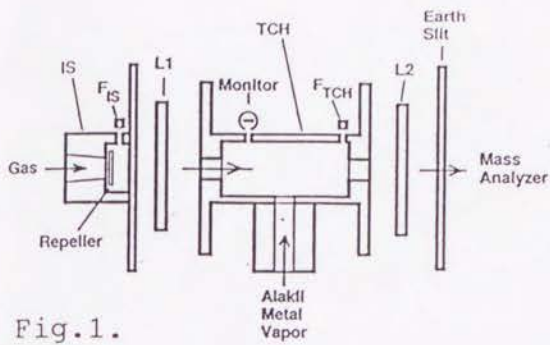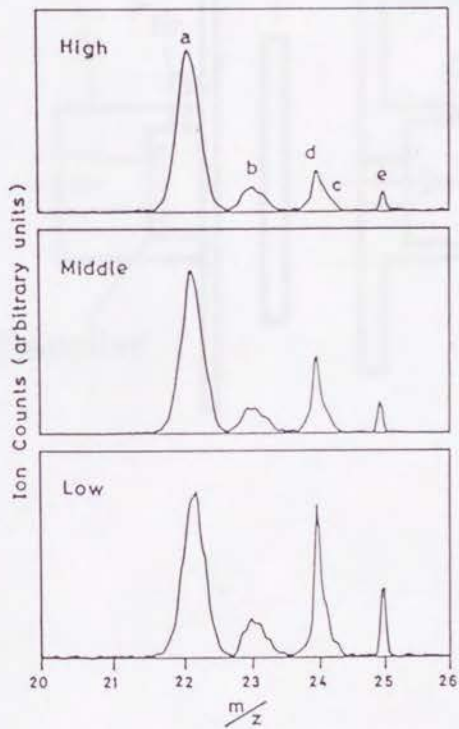Fig.5. Illustration of exothermicities of dissociative neutralization by single electron transfer. Energy values were derived from Table 3.
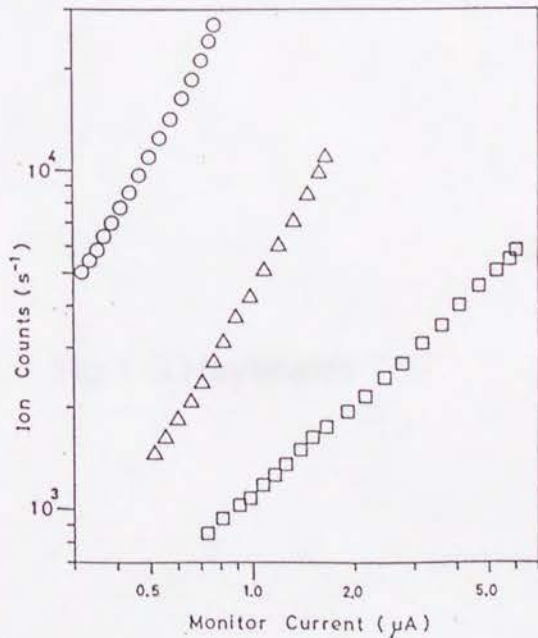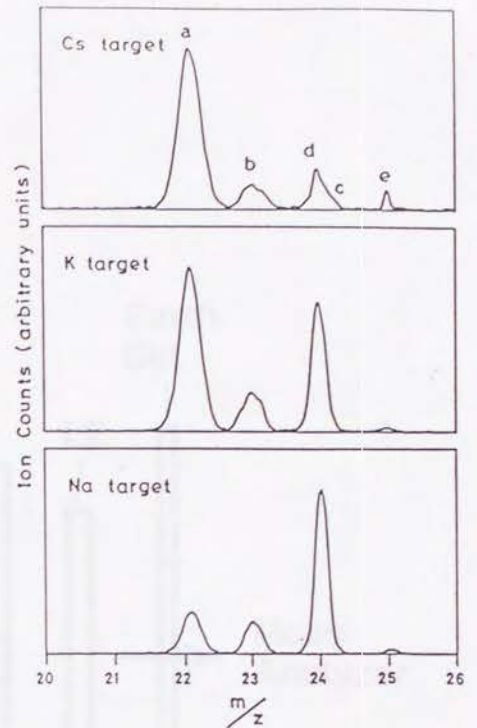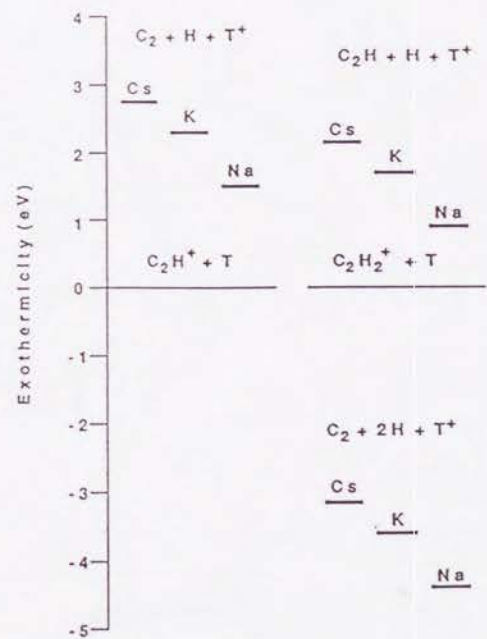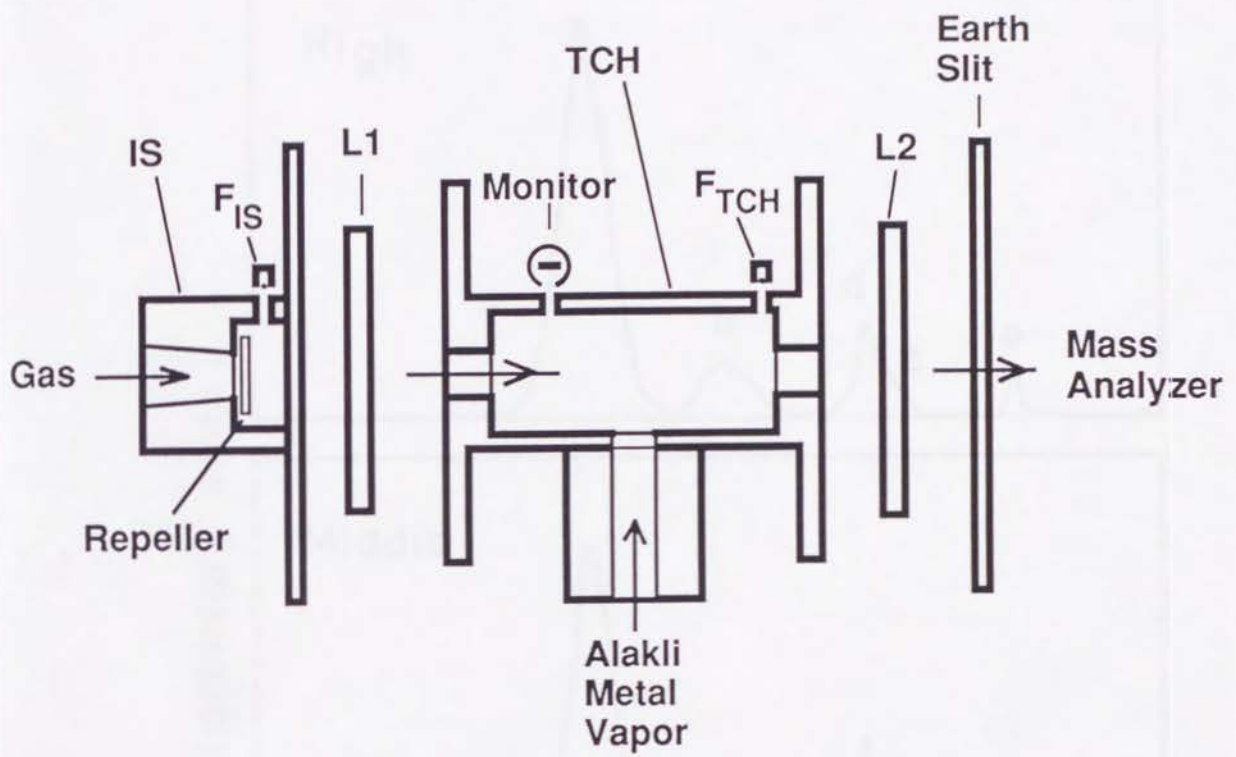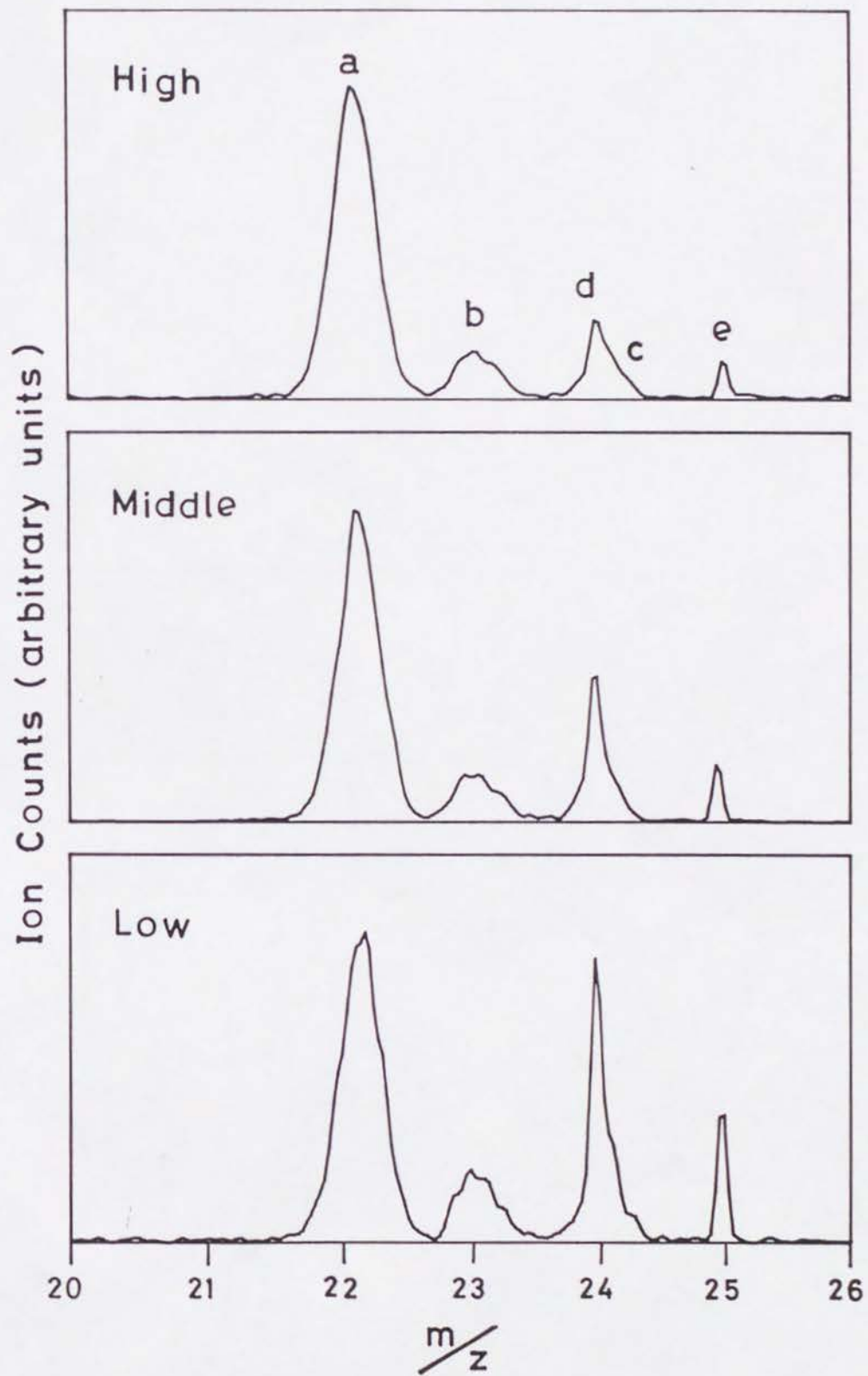
Fig.1.

Fig.2.

Fig.3.

Fig.4.
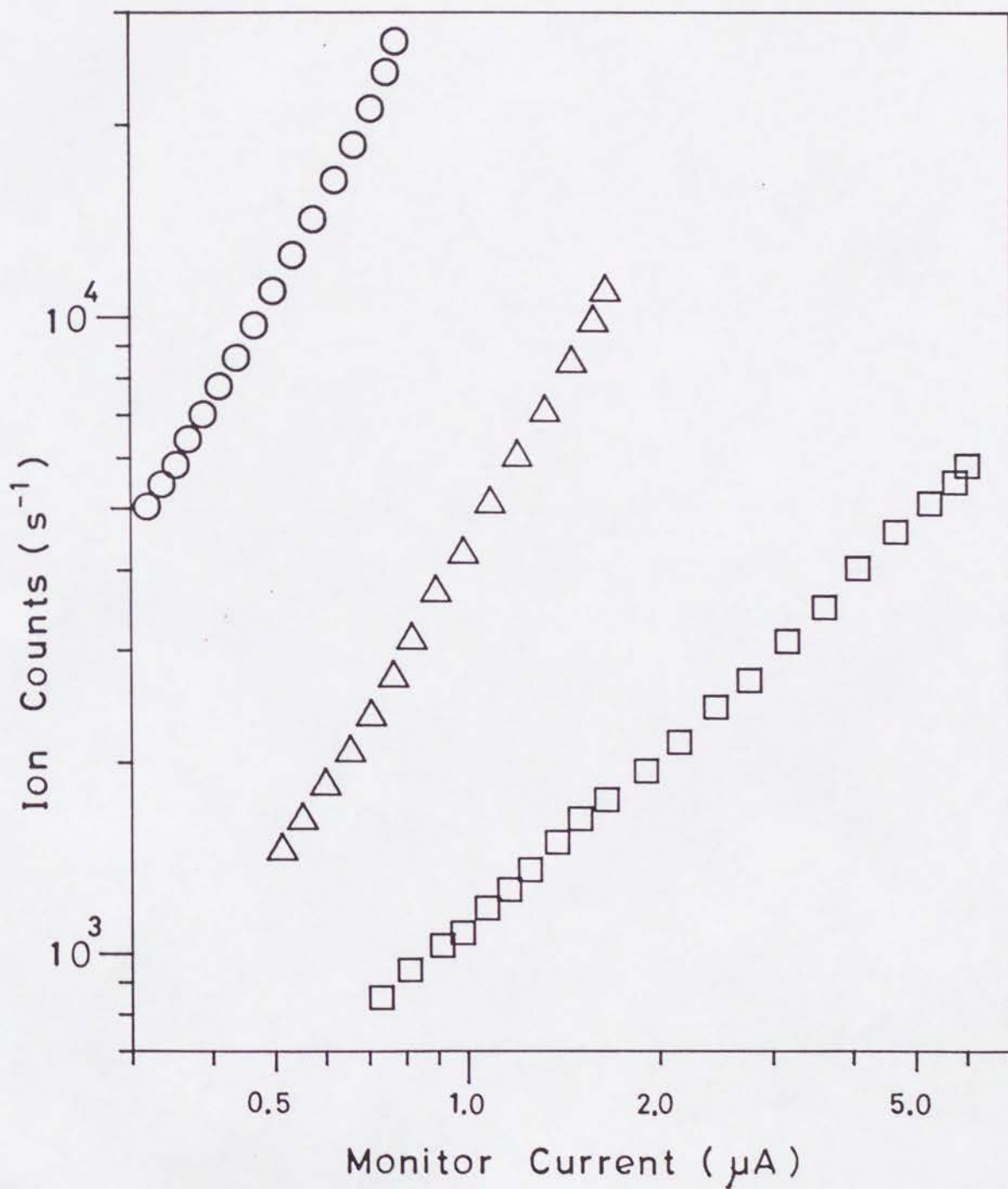

Fig.5.

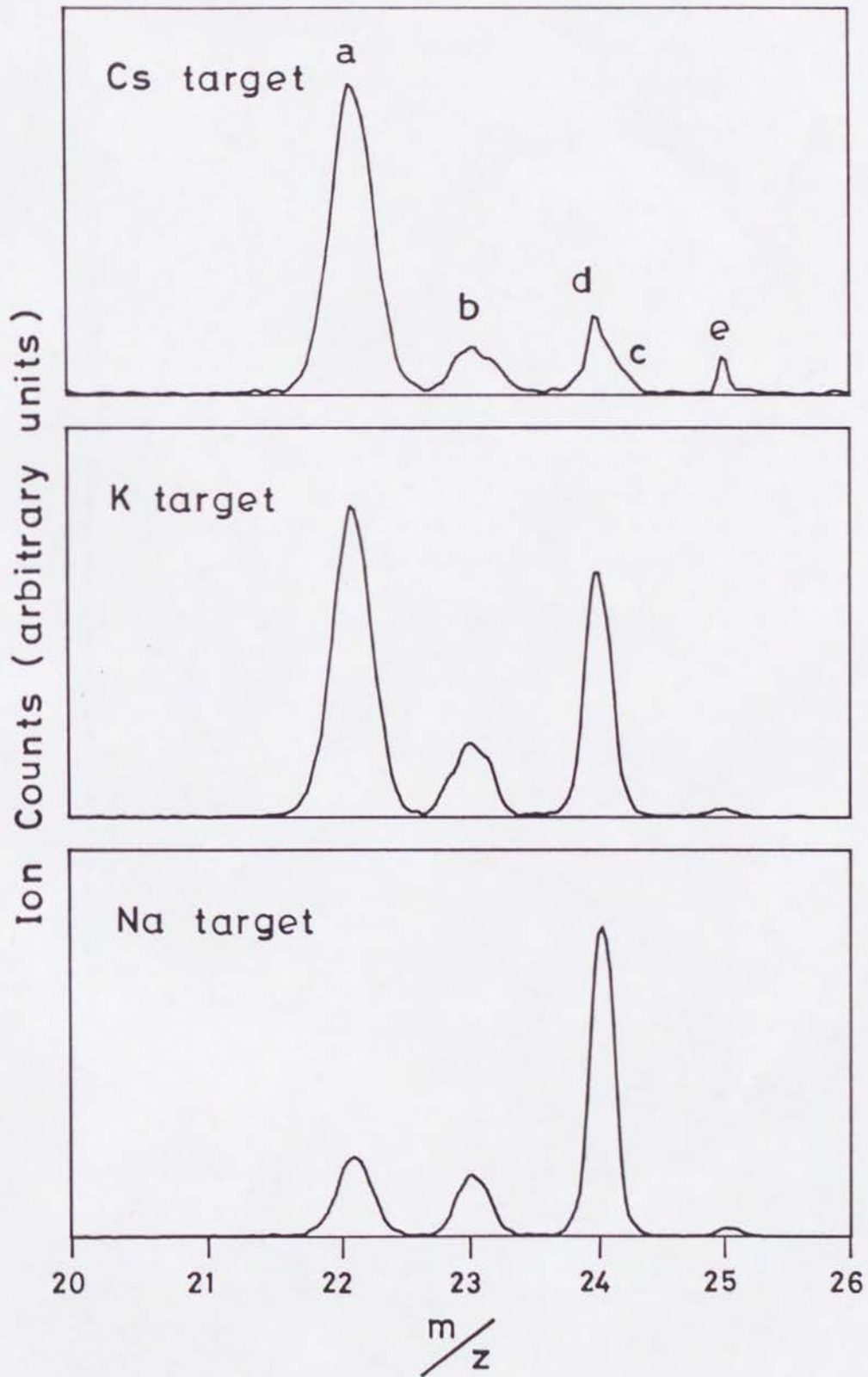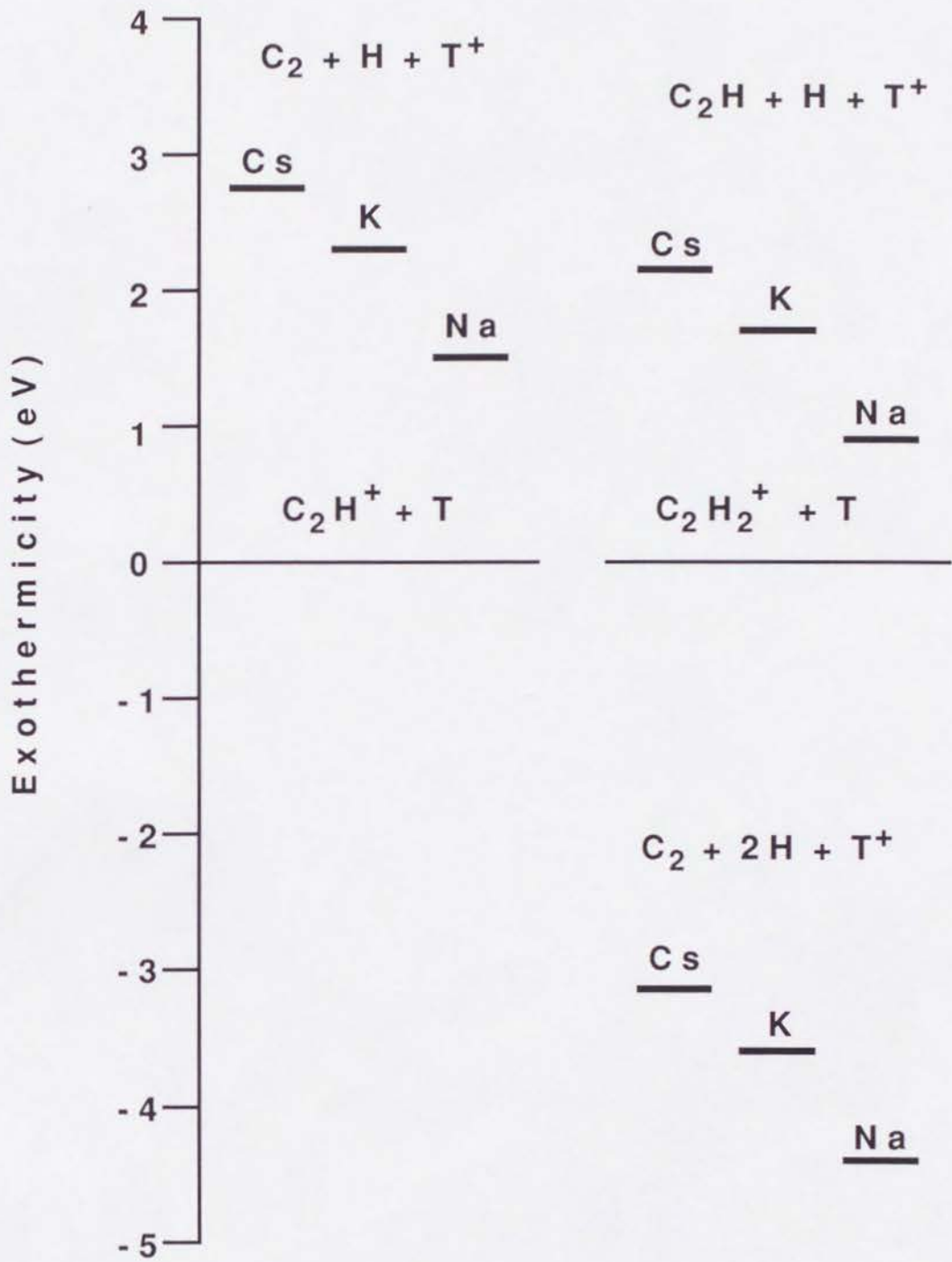Fig.1 S.Hayakawa

Fig.2

Fig 3

Fig.4

Fig.5

Table 1. Ionization potentials (IP), electron
affinities (EA) and bond energies (BE) of related
species in electron volts.

Species	IP	Species	EA
Cs	3.893	C_2H	2.969
K	4.339	C_2	3.269
Na	5.138		
C_2H_2	11.40	Bond	BE
C_2H	11.96	HC_2-H	5.34
		C_2-H	5.33

Table 2.   Reaction energies of each process for neutralization and anionization in electron volts.

Reaction Non-dissociative neutralization	Target Cs	K	Na
(1,6) $C_2H_2^+ + T \longrightarrow C_2H_2 + T^+$	7.51	7.06	6.26
(4) $C_2H^+ + T \longrightarrow C_2H + T^+$	8.07	7.62	6.82
Dissociative neutralization	Cs	K	Na
(3) $C_2H_2^+ + T \longrightarrow C_2 + 2H + T^+$	-3.16	-3.61	-4.41
(2,7) $C_2H_2^+ + T \longrightarrow C_2H + H + T^+$	2.17	1.72	0.92
(5) $C_2H^+ + T \longrightarrow C_2 + H + T^+$	2.74	2.29	1.48
Non-dissociative anionization	Cs	K	Na
(3,5) $C_2 + T \longrightarrow C_2^- + T^+$	-0.62	-1.07	-1.87
(7) $C_2H + T \longrightarrow C_2H^- + T^+$	-0.92	-1.37	-2.17
Dissociative anionization	Cs	K	Na
(1) $C_2H_2 + T \longrightarrow C_2^- + 2H + T^+$	-11.29	-11.74	-12.54
(2,4) $C_2H + T \longrightarrow C_2^- + H + T^+$	-5.95	-6.40	-7.20
(6) $C_2H_2 + T \longrightarrow C_2H^- + H + T^+$	-6.26	-6.71	-7.51

Table 3. Kinetic energy releases in eV obtained for the full width at half maximum of the peak. The value in the parenthesis shows the percentage of KER to the exothermicity.

| | Reaction | Target | | |
		Cs	K	Na
(a)	$C_2H_2^+ \longrightarrow C_2^-$	0.48 ± 0.04	0.39 ± 0.04	0.29 ± 0.04
(b)	$C_2H^+ \longrightarrow C_2^-$	1.07 ± 0.18 (39%)	0.66 ± 0.07 (29%)	0.49 ± 0.08 (33%)
(c)	$C_2H_2^+ \longrightarrow C_2H^-$	0.55 ± 0.06 (25%)	0.28 ± 0.03 (16%)	0.17 ± 0.02 (18%)

Table 4. Relative cross sections for the dissociative two electron transfer processes.

Reaction	Target Cs	K	Na
(a) $C_2H_2^+ \longrightarrow C_2^-$ / (b) $C_2H^+ \longrightarrow C_2^-$	1.28 ± 0.15	1.15 ± 0.38	0.51 ± 0.17
(a) $C_2H_2^+ \longrightarrow C_2^-$ / (c) $C_2H_2^+ \longrightarrow C_2H^-$	5.35 ± 1.29	1.89 ± 0.47	0.32 ± 0.08