Fragmentation of molecules under charge-changing collisions of a few MeV heavy ions

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Abstract. We investigated molecular fragmentation of CO and C$_2$H$_2$ molecules by impact of various fast heavy ions. Fragment ions produced in electron capture and loss collisions of projectile ions were measured in coincidence with final projectile charge states. Data acquisition using position sensitive detection system allows us to obtain 3D momentum imaging of fragment ions and kinetic energy release (KER) in various charge-changing collisions. It was found that the KER spectra show strong dependence on the type of charge-changing collisions. This may be caused by the difference of impact parameters associated with individual charge-changing collisions. Moreover we revealed the different fragmentation pathway between ion impacts and photoionization.

1. Introduction
Molecular fragmentation by a charged particle has been the subject of increasing attention to date [1-20]. In collisions with a fast heavy ion, a target molecule receives a considerable amount of electronic energy, leading to molecular excitation, fragmentation and multiple ionization as well. These processes are strongly dependent on the impact parameter between collision partners, molecular orientation and the type of projectile charge-changing. Hence acquisition of information about these quantities is important to achieve complete understanding of collision-induced molecular excitation and relaxation mechanisms. Recent and rapid development of multicoincidence and 3D momentum imaging techniques enables one to deduce important parameters such as molecular orientation before collisions [10, 12, 16, 17, 18], kinetic energy release (KER) of fragment ions [7, 8, 14, 15], molecular structure deformation prior to dissociation [9, 13, 20], and so forth. Investigation using these techniques extends from diatomic to polyatomic molecules including clusters and biomolecules [3, 4, 5, 6]. To date, however, collision induced molecular fragmentation using MeV energy heavy ions is not fully understood yet.

In this work, we study molecular fragmentation of CO and C$_2$H$_2$ induced by collisions with various fast heavy ions by means of a 3D momentum imaging technique. Fragment ions were measured in coincidence with the final projectile charge state. The present method allows us to determine the amount of KER in individual charge-changing collisions.
2. Experimental
Experiments were performed at the QSEC 1.7-MV tandem accelerator facility of Kyoto University. A schematic diagram of the experimental setup is shown in Fig. 1. The experimental apparatus and method are described elsewhere [7], and an essential outline is given here. A beam of A\(^{q^+}\) extracted from the accelerator was carefully collimated to about 0.1 mm in diameter and was charge purified with a magnetic charge-selector before entering a collision chamber. Here A\(^{q^+}\) stands for a projectile species with a charge state \(q\). Projectile ions used are 2.0 MeV Si\(^{2^+}\), 1.1 MeV O\(^{2^+}\) and 0.79 MeV B\(^{2^+}\) ions at the same collision velocity \(v=1.69\) a.u., and 6.0 MeV O\(^{4^+}\) ions at \(v=3.87\) a.u.. After passing through a gaseous jet target the projectile particles were charge-separated horizontally by an electrostatic deflector and detected by a movable solid state detector (SSD) with a rectangular entrance slit of 0.5mm \(\times\) 5 mm. Gaseous molecular jet targets investigated are CO and C\(_2\)H\(_2\). Fragment ions were extracted perpendicular both to the incident beam and the molecular beam and were detected by a position-sensitive delay line detector (DLD) [24]. Mass-to-charge of product ions was measured with a time-of-flight (TOF) spectrometer operated under a Wiley-McLaren spatial-focusing condition. Signals of fragment ions were recorded event-by-event in a digital oscilloscope (Wavepro7000, LeCroy) in coincidence with outgoing projectile ions. Measurements were carried out for one-electron capture collisions, one- and two-electron loss collisions as written, e.g. for CO, in the following way,

\[
A^{q^+} + CO \rightarrow A^{(q-1)^+} + CO^{r+} + (r - 1)e^- \quad (1\text{e-capture}) \\
\rightarrow A^{(q+1)^+} + CO^{r+} + (r + 1)e^- \quad (1\text{e-loss}) \\
\rightarrow A^{(q+2)^+} + CO^{r+} + (r + 2)e^- \quad (2\text{e-loss})
\]

Calibration of the time and the position of the detector was done by measurements of intact parent ions and the patterns of meshes placed in front of the detector, respectively.

3. Results and discussion
3.1. Fragmentation of CO
Figure 2 shows time-of-flight mass spectra from CO molecules measured in 2 MeV Si\(^{2^+}\) charge-changing collisions. One can see clearly that the intensity distribution of mass spectra differs strongly according to the type of charge-changing collisions. In 1e-capture collisions, an intact
ion CO⁺ is the dominant product, and fragmentation is suppressed significantly. This is because in a few MeV energy region an electron capture collision is a large impact parameter process, resulting in less fragmentation. By contrast, in electron loss collisions the mass spectra are dominated by fragment products. Electron loss collisions occur in close collisions, because the collisions need a large inelastic energy to remove a tightly bound projectile electron. In particular, 2e-loss from Si²⁺ needs ionization energies of at least 79 eV (= I₃ + I₄), and hence 2e-loss collisions are certainly limited to only close collisions. Such close collisions can induce large energy deposition into a target molecule, leading to fragmentation.

A typical example of two-dimensional TOF is shown in Fig.3, exhibiting correlations of fragment-ion pairs produced simultaneously. Fragment ions arising from various ion pairs such as (C⁺,O⁺), (C²⁺,O⁺), (C⁺,O²⁺), and (C²⁺,O²⁺) are well separated from one another. As reported in [7], these measurements allow us to deduce the branching ratios into individual fragmentation channels.

Figure 4 presents the KER spectra for CO fragmentation into various fragmentation channels in 2 MeV Si²⁺ collisions. The spectra exhibit considerable difference in loss and capture collisions, implying different excited states of CO⁺⁺ populated transiently. One can see that both the peak position and broadness become larger in 1e-loss collisions compared to 1e-capture. This behavior is caused by the difference of the effective impact parameters in these collisions, leading to a different energy transfer to a CO molecule. It should be noted again that in the case of electron loss collisions, distant collisions may be excluded but only small impact-parameter collisions are involved. Thus, electron loss collisions, particularly 2e-loss collisions, can lead to high degree of molecular excitation which results in larger kinetic energies as observed experimentally. On the other hand, the distant collision contribute largely in 1e-capture collisions.

Solid square curves are theoretical spectra estimated from a simple coulomb explosion model.
using the formula of $E_c = q_1q_2/R_e$, where $E_c$ is the central peak energy, $q_1$’s are the charges of ion pairs and $R_e$ is the equilibrium internuclear distance of CO. Following the theoretical investigation of potential energies of CO and CO$^+$ [28], the value of $R_e$ is nearly equivalent for neutral and ionized molecules. In this work, therefore, we assumed $R_e \approx 2.1 \pm 0.09$ a.u. for all these ion pairs. The width $W$ of the distribution is related to the probability density of the ground state of CO and may be estimated, to the first approximation, as follows [15].

$$W \simeq -\frac{dV}{dR} \delta R = \frac{q_1q_2}{R_e^2} \delta R$$

(4)

where $V(R)$ is the Coulomb potential between two particles and $\delta R = 0.18$ a.u. is the width of the internuclear distance of the ground state of CO [28]. The central energies $E_c$ of calculated KER spectra are close to the peaks of measured spectra, while the widths are completely different from experimental results. Invalidity of this simple model has already been reported in other experiments [14, 15]. It should be pointed out that this model does not hold even for the highest charge state (CO$^{4+}$), meaning that the potential energy cannot be approximated simply by a two-body Coulomb potential between C$^{2+}$ and O$^{2+}$. Estimated values of KER from potential energy curves of possible electronic states [12, 25, 26] are indicated by vertical lines. We found that the excited states of intermediate CO$^{2+}$ are mostly $1\Pi, 3\Sigma$ and $2^1\Sigma^+$, being consistent with other experimental results obtained for 11.4 MeV/u O$^{7+}$ [14]. In the case of CO$^{4+}$ fragmentation into (C$^{2+}, O^{2+}$) shown in (d), the KER spectra for 1e-loss and 2e-loss collisions are almost identical, implying equivalent excitation of CO ions in this fragmentation channel.

Figure 5 compares KER spectra in CO$^{2+} \rightarrow$ C$^+ +$O$^+$ obtained for 1e-loss and 1e-capture collisions of Si$^{2+}$, O$^{2+}$ and B$^{2+}$ ions with the same collision velocity of $v=1.69$ a.u.[7], and O$^{4+}$ ions at $v=3.87$ a.u.. When the impact velocities are the same, the KER spectra in 1e-loss collisions are larger than those of 1e-capture collisions irrespective of different projectile species. This trend is also found for N$_2$ fragmentation in charge-changing collisions of 300 keV Ar$^{5+}$ ions [19]. On the other hand, the KER spectra obtained for O$^{4+}$ ions ($v=3.87$ a.u.) are essentially the same for 1e- loss and capture collisions. This result indicates that the impact of 6 MeV O$^{4+}$ ions produces CO$^{2+}$ ions at equivalent impact parameters in both 1e-loss and capture collisions. In faster collisions of 97 MeV Ar$^{14+}$ ($v = 9.8$ a.u.) with CO [27], it was reported that the peak position of the KER in 1e-capture collisions is considerably larger than that in pure ionization.
CO\textsuperscript{r+} \rightarrow \text{C}^+ + \text{O}^+

1\Pi \ 3\Sigma^+ \ 2\Sigma^-

Coulomb Explosion Model

Figure 4. KER spectra in the fragmentation of CO\textsuperscript{r+} (r = 2, 3, 4) into various channels measured by 2.0 MeV Si\textsuperscript{2+} impact (v = 1.69 a.u.).

Figure 5. Comparison of KER spectra in various channels observed in charge-changing collisions of Si\textsuperscript{2+}, O\textsuperscript{2+}, and B\textsuperscript{2+} ions at v = 1.69 a.u., and O\textsuperscript{4+} ions from accurate potential surfaces \cite{12, 25, 26}. at v = 3.87 a.u.

of single electron. It was also found that multiple ionization and the degree of fragmentation are both enhanced largely even in 1e-capture collisions. Together with our experimental results, it is reasonably concluded that the impact parameter relevant to electron capture collisions becomes smaller with increasing collision velocity.

In electron loss collisions, it is interesting to see that all the KER spectra including O\textsuperscript{4+} impacts are nearly the same although the 1e-loss from O\textsuperscript{4+} certainly occurs in closer distant collisions compared with other projectile ions because of large ionization potential (I(O\textsuperscript{4+}) \simeq 114 eV). As discussed in \cite{8}, highly excited states may decay by an electron emission via autoionization. It implies that the electronic excitation energy may be saturated with increasing energy deposition into a molecule. The present result seems to support this saturation behavior.
3.2. Fragmentation of C$_2$H$_2$

Collision-induced fragmentation of polyatomic molecules opens several new relaxation channels such as emission of fragment molecular ions, bond rearrangement or structure deformation. Figure 6 shows the time-of-flight mass spectra of C$_2$H$_2$ molecules in 2 MeV Si$^{2+}$ impacts (v = 1.69 a.u.).

Predominant products are H$^+$, C$^r_\alpha$+ (r = 1, 2), CH$^+$, C$_2$+ and C$_2$H$^+$$_m$ (m = 1, 2). Moreover, molecular ions formed through bond rearrangement dynamics are also observed weakly; see the peaks of H$_2^+$ and CH$_2^+$. It is interesting to point out that the doubly charged parent ion (C$_2$H$_2$)$^{2+}$ is not observed in our collision condition, while this peak was observed rather strongly in 1.2 MeV Ar$^{8+}$ collisions [11]. It indicates that, in our fast lowly charged ion impact, (C$_2$H$_2$)$^{2+}$ may be formed to unstable electronic or vibrational excited states, leading to fragmentation. It was found that the mass spectra are strongly dependent on the type of charge-changing collisions. The dominant products are C$_2$H$^+$_m in 1e-capture, while those in 2e-loss collisions are CH$^+$_m produced through bond-breaking reactions. This fact also implies difference of effective impact parameters between capture and loss collisions.

Figures 7 presents KER spectra in fragmentation channels of C$_2$H$_2^{2+}$$^\ast$ → (C$_2$H$^+$, H$^+$). Two peaks at about 3eV and 5 eV may be assigned as the following fragmentation process [21]

$$\text{Si}^{2+} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2^{2+}\left(1^\Sigma_g^+\right) \rightarrow \text{C}_2\text{H}^+\left(3^\Pi\right) + \text{H}^+ \quad \text{(KER = 3eV)}$$ (5)

$$\text{Si}^{2+} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2^{2+}\left(1^\Pi_u^+\right) \rightarrow \text{C}_2\text{H}^+\left(1^\Delta \text{ or } 1^\Sigma\right) + \text{H}^+ \quad \text{(KER = 5eV)}$$ (6)

We found that in fragmentation channel of (C$_2$H$^+$, H$^+$), the KER spectra do not strongly depend on the charge-changing collisions. Our spectra also revealed that above two electronic states $1^\Sigma_g^+$ and $1^\Pi_u^+$ are involved in this fragmentation channel, in consistent with previous soft X-ray experiments [21]. It was found that the excited state $1^\Pi_u^+$ may be observed only in 2e-loss collisions.
Figure 7. KER spectra in a fragmentation channel (C$_2$H$_2$+,H$^+$) obtained for 2MeV Si$_2^+$ collisions ($v$=1.69 a.u.) with C$_2$H$_2$.

Figure 8. The same as in Fig. 7 but for fragmentation channels (C$^+$,C$^+$), (C$^+$,CH$^+$) and (CH$^+$,CH$^+$).

collisions. It indicates that the excited state, such like $^1\Pi_u^+$, may be preferentially created by close collisions.

KER spectra for C-C bond broken fragmentation channels are presented in Fig. 8. The KER spectra for (CH$^+$,CH$^+$) show little dependence on the projectile charge-changing collisions. The peak position is about 3 eV. This is in agreement with the previous work by 1.2 MeV Ar$^{8+}$ impacts [11]. On the other hand, the peak position of KER is found to be about 6.5 eV in photo-doubleionization studies using soft X-rays [21], VUV photons [22] and intense IR lasers [23]. It is interesting to point out that, in these investigations, the mechanisms of double ionization of molecules are different from each other. In the case of soft X-ray irradiation [21], C 1s photoionization occurs first and then C K-VV Auger decay takes place, resulting in the formation of double ionized C$_2$H$_2$ molecules. They measured fragment ions in coincidence with Auger electrons and doubly ionized states decaying into (CH$^+$,CH$^+$) were assigned as follows.

\[
C_2H_2^{2+}(^1\Pi_u^+) \rightarrow CH^+(^1\Sigma) + CH^+^{*}(^1\Pi) (KER=6.5eV)
\]  

(7)

On the other hand, the double ionization is induced by one-photon absorption in VUV irradiation and by multi-photon processes in intense IR lasers. In our ion-impact experiments, the peak values of KER are smaller than those in photoionization, indicating lower electronic excited states compared to the case of photoionization [21]. Zyubina et. al. predicted that the ground triplet electronic state with ground vibrational state of C$_2$H$_2^+$ decays mostly to (C$_2$H$^+$,H$^+$) rather than (CH$^+$,CH$^+$), while it decays strongly to (CH$^+$,CH$^+$) when the vibrational states are
excited [29]. In order to interpret our experimental results of small KER, we speculate, therefore, that ion impacts produce the ground electronic state but with highly vibrational excitation of \(C_2H_2^+\). The KER spectra in C-C bond broken fragmentation channels become broader and tailing to higher energies with increasing loss-number of hydrogen atoms. The results indicate clearly that the (C\(^+\), C\(^+\)) channel is attained through many intermediate dissociation channels compared to other two channels retaining C-H bonds. If the coulomb explosion model is applied to the (C\(^+\), C\(^+\)) channel, the mean value of KER estimated from 14.4/R [eV/\(\text{Å}\)] with \(R = 1.2 \, \text{Å}\) between two C\(^+\) ions is about 12 eV, being obviously inconsistent with the experimental KER. It implies that the binary explosion model seems to be ruled out. One possible reason is the charge-screening effect by bonding electrons which are largely located in between two carbon atoms, resulting in smaller KER than the binary explosion model. Information is needed about accurate potential surfaces, taking account of the screening effect, in order to reproduce the KER spectra.

4. Summary

Brief description is given for our recent experimental data concerning molecular fragmentation of CO and C\(_2\)H\(_2\) in charge changing collisions of fast heavy ions by means of 3D momentum imaging techniques. The kinetic energy distribution of fragment ions provides information about transient molecular excited states. The KER spectra show strong dependence on the type of charge-changing collisions. This may be caused by the difference of impact parameters associated with individual charge-changing collisions. We also found the mean KER to be much smaller than that obtained in photoionization experiments, indicating different fragmentation pathways between ion impacts and photoionization.

Acknowledgments

The work supported by Quantum Science and Engineering Center of Kyoto University. We are grateful for valuable discussion with Dr. H. Tsuchida, Dr. T. Majima and Dr. Y. Nakai.

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