Collision Dynamics In Low Energy Collisions Of Multiply Charged Ions With Molecules

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Abstract. Combination techniques of the Mini-EBIS and OPIG have been used for cross section measurements of multiply charged ions and for study of collision dynamics in multiply charged ion-molecule collisions. The general features of single- and multiple-charge changing cross sections measured at low energies below 1 keV per charge and some topics of collision dynamics in multiply charged ion-molecule collisions studied by a new multi-coincident technique are presented.

INTRODUCTION

In the last two decades, the advance of source devices has promoted the study of charge transfer in collisions of multiply charged ions (MCIs) with atoms and molecules. Accurate determination of cross sections and elucidation of collision dynamics for charge transfer of MCIs in low energy collisions with atoms and molecules are important ingredients for understanding various applications in applied sciences and technologies such as the research of ionosphere, the study of molecular synthesis in the interstellar space, astrophysical plasmas [1] and laboratory plasmas for fusion research [2]. At present, however, there is a scarcity of experimental and theoretical studies in the low energy region below 1 keV.

In low energy collision experiments, not only preparation of an intense ion beam can be interrupted by space charge, stray fields etc., but also perfect collection of product ions becomes difficult due to the dispersion of scattering angle after collisions. In order to measure charge transfer cross sections of MCIs, the next issue is how to provide a stable beam of slow MCIs with a narrow energy spread. Furthermore, in order to investigate collision dynamics of MCIs in collisions with molecules, development of multi-coincidence technique is required to clarify complicated processes in ion collision-induced fragmentation of molecules.

Teloy and Gerlich [3] developed a beam guide technique for thermal collision experiments. We applied the technique to beam experiments at energies higher than the thermal region and proved that the octo-pole ion beam guide (OPIG) is an ideal tool for low energy collision experiments [4, 6, 7]. The structure of the OPIG is simple, which consists of eight parallel poles equally spaced around an axis, and the operation of the OPIG is easy, where oscillatory R-F voltages of $\pm V \cos(\omega t)$ are supplied to poles alternatively in opposite phase. The oscillating R-F field modulates and confines only the radial motion of charge particles and never affects the drift
motion along the axis. The OPIG is of great advantage for transportation and confinement of charge particles. It is available for various uses such as a collision cell, a time-of-flight (TOF) drift tube, a liner trap, an ion guide through a differential-pumping region and so on.

In 1987, in order to investigate charge transfer of MCIs in the low energy region, we developed a small electron beam ion source (Mini-EBIS) based on a new idea of cooling magnetic solenoid coils with liquid nitrogen [5, 6]. The Mini-EBIS can provide a stable MCI beam with a narrow energy spread in the operation mode of the DC ion extraction, where a suitable potential barrier is set at the exit of ionization region and its adjustment makes possible not only to improve charge distribution of MCI but also to reduce energy spread of ion beam extracted from Mini-EBIS. Usually contamination of metastable ions causes a very troublesome problem in cross section measurements. Also, the DC mode operation of the Mini-EBIS is very effective to suppress production of excited ions with a long life because the excited ions can be quenched during long ion-confinement time in the DC operation mode. Practically, no existence of long-lived excited ions has been found in MCI beams extracted from the Mini-EBIS except for low charge state ion beams of C^{2+} and O^{2+}.

Thus, using both techniques of the OPIG and the Mini-EBIS, single- and multiple-charge changing cross sections for various MCI collision systems successfully have been measured in the low energy region of .5 eV to 2000 eV per charge where experimental cross data is very scarce [4, 6, 8-16].

Recently, we have developed a new experimental method using multi-coincidence technique to study collision dynamics in MCI-molecule systems [17]. In this method, coincidence measurements of two TOF spectra for fragment ion pair exploding in opposite directions are coupled with the angle resolved energy gain spectroscopy for projectile ions after collisions. Various sets of collision parameters needed to elucidate dynamics in MCI-molecule collisions are readily available in the multi-coincidence experiment.

In this paper, characteristic features of cross sections measured for charge transfer of MCIs in the low energy region and some topics of collision dynamics for MCI-molecule systems will be reported.

**CHARGE-CHANGING CROSS SECTIONS IN LOW ENERGY COLLISIONS OF MULTIPLY CHARGED IONS**

**Cross Section Measurements using the OPIG and the Mini-EBIS**

Both techniques of the OPIG and the Mini-EBIS have been applied in cross section measurements for charge transfer of MCIs in low energy collisions with atoms and molecules. A schematic diagram of the experimental setup constructed for the cross section measurements is shown in Fig.1. Details of the experimental setup and procedure have been described previously [4, 6, 7]. In brief, primary multiply charged ions extracted from the Mini-EBIS are mass-analyzed by the first electromagnetic \( m/lq \) analyzer and decelerated down to a desired collision energy, and injected into the
OPIG in the collision cell which contains the target gas. Primary and target ions leaving from the OPIG are accelerated again and identified by the second electromagnetic $m/q$ analyzer. The collision energy is determined by potential difference between the ion source and the collision cell. The cross sections are determined from the initial growth of product ion intensity with increasing the target gas pressure under the single collision conditions. In the present measurements, since product ions are identified by $m/q'$ for the final charge state of $q'$, measured cross sections of $\sigma_{q,q'}$ for charge-changing from $q$ to $q'$ correspond to sum of the pure electron capture cross section of $\sigma_{q,q'}$ and the transfer ionization cross sections of $T_{q,q'}$ for the Aüger processes in which the projectile ion captures ($q-q''$) electrons from the target and releases ($q'-q''$) electrons.

\[
A^{q+} + B \rightarrow A^{q'+} + B^{(q-q')^+} \quad \sigma_{q,q'}
\]

\[
A^{q+} + B \rightarrow A^{q'+} + B^{(q-q''+}
\downarrow \text{Aüger processes}
\]

\[
A^{q'+} + (q'-q'')e \quad \sigma_{q',q''}^{T}
\]

\[
\sigma_{q-q''} = \sigma_{q,q'} + \sum_{q''} \sigma_{q'',q'}^{T} \quad (q'' < q' < q)
\]

By application of the OPIG and the Mini-EBIS, single- and multiple-charge changing cross sections of MCIs in collisions with atoms and molecules have been measured systematically in the low energy range of 0.5 to 2000 eV per ion charge [4, 5, 8-16]. The overall uncertainty of measured cross sections is $\pm 25\%$ commonly, which mainly results from systematic errors in determination of the target density and the collision length. Uncertainty of the collision energy is $\pm 0.5 \times q$ eV in the whole energy range measured.

**FIGURE 1.** Schematic diagram of experimental setup for cross section measurements
Charge Changing Cross Sections of MCIs at Low Energies

Single- and multiple-charge changing cross sections measured at low energies below 1 keV were reported in [5] for C^{4+}, N^{4+} and O^{4+}-He systems, in [12] for I^{q+}(q=24-26)-He systems, in [11, 12, 13] for Ar^{q+}(q=6-9)-He and H_{2} systems, in [16] for C^{q+}, N^{q+} and O^{q+}(q=2-9)-He and H_{2} systems, in [10] for C^{4+}-CH_{4}, C_{2}H_{6}, C_{3}H_{8} and n-C_{4}H_{8} systems, in [13] for C^{4+}-Ne, Ar and Kr systems, in [14] for Ar^{q+}(q=3-9)-Ne systems, in [15] for Kr^{q+}(q=3-9)-Ne and -CO systems and for Kr^{8+}-N_{2} and O_{2} systems, in [8] for He^{2+}-He and H_{2} systems, and in [15] for He^{2+}-N_{2}, O_{2} and CO systems, previously. From these systematic cross section measurements, following characteristic features have been found at low energies below 1 keV.

1. Almost of all measured cross sections increases with decrease of collision energy at low energies. As seen in Fig.2, interpolation between the present σ_{1} data and the near-thermal-energy data [17] in Ar^{6+}-H_{2} would reveal an increasingly better agreement of the experimental results with the Langevin cross section which is in reverse proportion of square root collision energy. This trend seems to support that the charge transfer collision is dominated by induced-dipole potential at enough low energies.

2. In collisions of MCI with many electron targets, contributions of multiple-charge changing processes become more significant and their cross sections strongly depend on the collision energy as to take a minimum. With increasing number of electrons transferred from the target to the projectile, the structure of the minimum
becomes deeper and its energy position shifts towards the higher energy side as seen in Fig.3.

3. As seen in dash-and-dotted curves in Fig.2, an extended classical over barrier model taking accounts of the orbiting effect due to the induced-dipole polarization well reproduces energy dependence of measured cross sections, qualitatively. In this model, the model cross section of $\sigma_{ECOBM}$ is given by

$$\sigma_{ECOBM} = \sum b^2_i - b^2_i = \sum (r_{i+1}^2 - r_i^2) \left(1 - \frac{\alpha q^2}{2E_{cm} r_i^2 r_{i+1}^2}\right)$$

at energies of which interaction ranges of $r_i$ and $r_{i+1}$ effective for related charge transfer channels are larger than the orbiting radius of $r_0 = (\alpha q^2 / 2E_{cm})^{1/4}$, where $\alpha$ is a polarizability of the target, $q$ is a charge state of the projectile and $E_{cm}$ is collision energy in the center-of-mass systems. Decreasing collision energy, energy dependence of the cross section changes to increasing in proportion to $E_{cm}^{-1/2}$ as $r_0$ becomes larger than $r_i$.

4. Molecular target makes much contribution to lead multi-electron transfer and gives larger cross sections rather than atomic targets, especially at low energies. As results, energy dependences of cross sections for molecular targets are weaker than those for atomic targets as seen in Fig.3.

Thus, it is concluded that the typical energy dependence of charge changing cross sections in MCI collisions will be decided by competition between the orbiting radius and interaction ranges effective for related charge transfer channels. In the MCI-molecule collisions, it is a great interest to know how molecular targets explode in respective multi-charge changing reaction processes.
STUDY OF COLLISION DYNAMICS FOR MCI-MOLECULE SYSTEMS

Setup for Multi-Coincidence Experiments

In order to investigate dynamics in MCI-molecule collisions, we have developed a new experimental method using multi-coincidence techniques [18-19]. Setup of a constructed apparatus is shown in Fig.4. The beam of MCI extracted from the Mini-EBIS collides with molecules effused from a nozzle in the field free region, fragment ions are measured by two TOF analyzers installed in both sides and the energy and scattering angle of MCI after collisions are measured by a position sensitive detector (PSD) of a parallel plate type energy analyzer. Here, OPIG is used as a TOF drift tube. In this setup, fragment ions and projectile ions scattered on a fixed collision plane are simultaneously detected for respective collision events. This is essentially effective not only to improve efficiency of coincident detection but also to simplify analysis of collision dynamics.

Collision Dynamics of MCI-Molecule Systems

In the present multi-coincidence experiments, fragmentation processes and their branching ratios in double electron capture collisions of $^3\text{He}^{2+}$ with H$_2$, N$_2$ and CO and the kinetic energy release (KER) distribution of each fragment ions have been successfully examined [18], and details of collision dynamics in Kr$^{8+}$-N$_2$ and CO collisions have been revealed [19]. Here, some topics of experimental results for Kr$^{8+}$-N$_2$ collisions are presented briefly.

All of reaction processes occurring in Kr$^{8+}$-N$_2$ collisions are easily resolved from a coincidence map of two TOF spectra of fragment ions triggered by same signal of charge-selected projectile ion. In (a), (b) and (c) of Fig.5, two TOF spectra of fragment ions triggered by Kr$^{7+}$, Kr$^{6+}$ and Kr$^{5+}$ ions produced in collisions of Kr$^{8+}$ with N$_2$ at
171 eV/amu are indicated at upper and left sides, their coincidence components are plotted in two-dimension area and the two-dimensional coincidence signals are projected in the upper and left sides again. Collision parameters of scattering angle, reaction energy and recoiled momentum are derived from angle-resolved energy gain spectroscopy of related projectile ions. As an example, raw data of angle-resolved energy gain distributions of projectile ions selected for related single-charge changing processes are demonstrated in Fig. 6. Furthermore, true values of the kinetic energy released (KER) distributions in the collision-induced fragmentation of molecules can be derived from either angle-resolved energy gain data or momentum distributions of fragment ion pairs observed in the coincidence TOF spectra using recoiled momentum and reaction energy determined above.

Thus, single-, double-, triple- and fourfold-charge changing processes of Kr\(^{8+}\) ions in collisions with N\(_2\) molecules are resolved as follows.

\[
\begin{align*}
Kr^{8+} + N_2 & \rightarrow Kr^{7+} + N_2^+ + Q(\approx 15 \text{ eV}) \\
& \rightarrow Kr^{7+} + N_2^+ + e^- + Q(\approx 30 \text{ eV}) \\
& \rightarrow Kr^{7+} + N^+ + N^+ + Q \\
& \rightarrow Kr^{7+} + N^+ + N^+ + e^- + Q(=25 - 35 \text{ eV})) \\
\end{align*}
\]  

Figures 5, 6. Two TOF spectra of fragment ions and their coincidence maps in Kr\(^{8+}\)-N\(_2\) collisions at 171 eV/amu. (a), (b) and (c) are triggered by product ions of Kr\(^{7+}\), Kr\(^{6+}\) and Kr\(^{5+}\), respectively.

Figure 6. Raw data of angle-resolved energy gain distributions of product Kr\(^{7+}\) ions measured in coincidence with formations of N\(_2^+\), N\(_2^{2+}\), N\(^+\)+N\(^+\) and N\(_2^+\)+N\(^+\) in single-charge changing collisions of Kr\(^{8+}\) with N\(_2\) at 48 eV/amu.
From related coincidence TOF spectra, it has been revealed that many electron capture processes followed by emission of some electron contribute to each charge changing collision of Kr\(^{8+}\)-N\(_2\) system. However, we cannot determine whether these
electrons are emitted from the projectile or the target. Considering the energy matching between possible initial and final channels, these electrons are likely to be emitted by the Auger process of the projectile.

In coincidence measurements of two TOF spectra triggered by charge-selected projectile ions, three interesting collision phenomena are found. The first is named as “peak-shifting”, in which peak positions of molecular ions in TOF spectra measured for single-charge changing collisions shift to high energy side with decreasing collision energy as seen in Fig.7. The others are of ion pair formation peaks and named as “peak-splitting” and “anisotropic splitting”. As seen in Fig.8 which shows three-dimensional plots for the coincidence map of two TOF spectra triggered by Kr\textsuperscript{6+} ions in Kr\textsuperscript{8+}-N\textsubscript{2} collisions at 171 and 19 eV/amu, all fragment ion pair peaks split into two peaks of a couple of “the fast ion” and “the slow ion” with decreasing collision energy and asymmetric charged fragment peaks of them unevenly split so as charge state and intensity of the fast ion are larger than those of the slow ion. Both phenomena of the “peak-splitting” and the “anisotropic splitting” are enhanced with decreasing collision energy and the intensity unbalance observed for asymmetric charged split peaks (i.e. the “anisotropic splitting”) becomes more significant with degree of the charge unbalance of fragment ions. The fast ion with larger charge trends to align at the far side of MCI and to proceed forward the riches of the fast ion with decreasing collision energy, and then the alignment faced MCI seems to be almost fully oriented at low energies below 10 eV/amu. The reaction energy and scattering angle distribution of asymmetric charged fragmentation processes are almost independent of the orientation.

According to kinematics assuming the conservation rules of energy and momentum, every collision dynamics of related reaction processes has been proved experimentally as the transverse recoil momentum $P_\perp$ and the scattering angle $\Theta_{\text{cm}}$, in the center-of-mass frame are approximately in reverse proportion to a square root of collision energy $E_0$ and to collision energy $E_0$, respectively. The phenomena of “peak-shifting” and “peak-splitting” are originated from the collisional momentum transferred from the projectile to the target. The velocities of the fast and slow ions are determined by KER and transverse recoiled momentum. In this coincidence experiments, if the fragmentation is isotropic, both intensities of the fast and slow ions should be balanced even for asymmetric charged fragmentations. Thus, the
“anisotropic splitting” phenomenon observed for the case of asymmetric charged fragments gives us an evidence that the fragmentation of multiply charged molecular ions is oriented. We suppose the anisotropic fragmentation is closely connected with the polarization effect of electrons in the target molecule and the more complete clarification of the “anisotropic shifting” phenomenon will lead us a deep understanding of the charge transfer mechanisms in MCI-molecule collisions.

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