Charge-sharing in fragmentation of nitrogen molecules in collision with highly charged ions

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Abstract. An apparatus for low-energy collision of highly charged ions with molecules, comprising a position sensitive time-of-flight measurement devise for recoil ions and a charge state analyser for the scattered projectile, was newly constructed at a beam line of an electron cyclotron resonance ion source. Collision experiments of 120 keV Ar8+ with the target of nitrogen molecules were conducted as a test run of this apparatus. Focusing on the dissociation channels with asymmetric sharing of the charges by fragmentation, correlation between Auger electron emission of the projectile and Coulomb explosion of the target is discussed.

1. Introduction
When homonuclear diatomic molecules are highly ionized by low-energy collision of highly charged ions (HCI), total charges of the transient molecular ions are eventually shared by the dissociating fragments mainly in the way that these are distributed equally, or near equally with a single charge difference [1]. This is simply understandable in terms of energetics that such sharing minimizes the total ionization energy. In covalent molecules, valence electrons are delocalized, and charge-rearrangement on the way of fragmentation tends to reduce the charge inequality. Nevertheless, highly-asymmetric channels have been observed to some extent, and have attracted attention since the information at the instant of collision may be preserved in such events. It is natural to expect that the asymmetric channels are sensitive to the electron capture conditions, orientation of the target and the impact parameter. Aside from the experimental difficulties, the orientation effect and the impact parameter are measurable. In fact, a sharp orientation preference has been found for rare-gas dimer target [2], although it is an exceptional case in which asymmetric sharing is a major channel [3], most likely due to low mobilities of electrons in the dimer. The question is whether it can be observed for covalent molecules.

To observe the orientation effect, difficulty arises in detection efficiency of lower charged fragments in addition to that caused by small branching ratios of highly charge-asymmetric channels. Generally speaking, fragment ions with large velocity components perpendicular to the TOF axis tend to escape from the detection area. For (near) symmetric channels, the charge states of the energetic fragments are high since these are produced from highly charged parent ions, for example, by the reaction (N₂)⁵⁺ → N³⁺ + N²⁺. In such cases, TOF of the ions are small and radial drift length is relatively small. On the other hand, lower charge fragment in highly asymmetric channel, for example N¹⁺ formed in (N₂)⁶⁺ → N⁴⁺ + N¹⁺, has a large TOF with large coulombic energies, and the radial drift length will be larger. Thus, we need a large detector or sophisticated ion optics for this purpose. As for
the impact parameter, number of Auger electrons emitted from the scattered projectile can be a rough measure. For example, triple capture collisions may lead to single and double Auger emission processes, in which the latter is considered to be the processes with larger impact parameter. 

Recently, we reconstructed a new beam line of the electron cyclotron resonance (ECR) ion source at Tokyo Metropolitan University. A cross-beam apparatus was installed for the study of electron capture dynamics of HCl with a molecular target. In this paper, we describe the details of the test experiments and discuss the preliminary results.

2. Ion-molecule collision apparatus

A schematic drawing of the collision apparatus is shown in figure 1. The apparatus is basically combined from the two existed ones comprising a position-sensitive time-of-flight (PSTOF) device with a large position-sensitive detector (120 mmφ) [4] and a charge analyzer for scattered projectile ions [5]. It allows us to observe highly charge-asymmetric dissociation channels correlated with different number of Auger electrons. The HCI s produced in a 14.25 GHz ECR ion source are extracted and introduced to the apparatus typically with the energy of 15q keV. The ion beam is trimmed by two 1 mm-pinholes and controlled by two sets of deflectors. The target molecules are first introduced to a beam source chamber evacuated by a 1500 L/s turbo molecular pump, and then trimmed by a skimmer and directed to the collision chamber evacuated by a 400 L/s turbo molecular pump. For a condensable target, a liquid nitrogen trap assists the evacuation. At the collision center, the HCI beam was crossed with the target molecular beam at the right angle.

After the collision, the scattered projectiles are dispersed according to the charge states by a set of deflectors, and detected by an MCP with a position-sensitive anode. To select desired charge state, first the positional image is acquired. A typical image obtained for Ar8+ collision with N2 is shown in the inset of the figure 1, in which the spots of the scattered ions with different charge states are reasonably separated. Then, the center of the desired spot is selected by the four-jaw slit to avoid contamination of ions with the neighboring charge. Detection of the charge-selected scattered ions is used as a TOF trigger for the recoil ion measurement. The fragment ions from highly-charged molecular ions are extracted by a homogeneous electronic field. The TOF spectrometer consists of a stack of 30 electrodes carefully designed so as to minimize the inhomogeneity of the electric field [4]. From the event-by-event multi-hit PSTOF data stored in the list mode, we extract relevant coincidence events to determine the velocity components of all the fragment ions.

In the present study, 120 keV Ar8+ ions were used as projectiles. The velocity of the projectile ions is about 0.40 a.u., where multiple electron capture occurs dominantly rather than ionization does. The typical operating pressure of the nitrogen molecular beam was $8 \times 10^{-4}$ Pa, while the base pressure was $5 \times 10^{-7}$ Pa, in the collision chamber. The electric field applied to the TOF tube was 15.1 V/mm. To calculate the velocity vectors of the fragments, the momentum conservation rule was imposed on each fragment pair while a momentum transferred by the projectile was neglected. The distance from the collision point to the detector calculated in this way ranges from 199 to 209 mm, agreeing with the
mechanical configuration. Then, kinetic energy releases (KER) of the ion-pair fragmentation channels were obtained.

3. Results and discussion

The coincidence map of the nitrogen molecules with the trigger of scattered Ar$^{6+}$ is shown in figure 2, by which the fragmentation channels N$^{p+}$-N$^{q+}$: (p, q) = (1, 1), (1, 2), (1, 3), (1, 4), (2, 2), (2, 3), (2, 4), (3, 3) are identified. Since the events are correlated with scattered Ar$^{6+}$, the initial projectile Ar$^{8+}$ ions capture two- to six-electrons, and then the transient ions de-excite accompanying zero- to four-Auger electron emission, while the highly-charged nitrogen molecules dissociate:

$$\text{Ar}^{8+} + \text{N}_2 \rightarrow \text{Ar}^{(8-n)+} + \text{N}_2^{n+}$$

For Ar$^{5+}$ (the figure is not shown here), the channels (p, q) = (1, 2), (1, 3), (1, 4), (2, 2), (2, 3), (2, 4), (3, 3), (3, 4) are also identified with emission of from zero- to four-Auger electrons. As can be seen in the figure, some spots are partly hidden by the degenerate TOFs, and some spots overlap with each other. In such cases, we have to extract the events within a specific range of orientation with respect to the TOF axis. In the present study, we analyze the charge asymmetric dissociation channels with no such problems.

For (1, 2), (1, 3) and (1, 4) channels, the KER distributions were derived from the double-hit PSTOF data, triggered by Ar$^{6+}$ and Ar$^{5+}$. The numbers of emitted Auger electrons are therefore one to three for Ar$^{6+}$ and zero to two for Ar$^{5+}$. The results are summarized in figure 3. A striking difference among the channels appears in the peak energies, that is, irrespective of the number of Auger electrons, the peak positions of the KER distributions for higher-asymmetric fragmentation channels (1, 3) and (1, 4) are much larger than those estimated from the Coulomb explosion (CE) model, while the positions for near-symmetric (1, 2) ones are around the CE value. In general, higher peak values and broader distributions of the KER are considered to be outcomes of production of highly excited electronic states at the time of the electron removal. Thus, the results suggest that the asymmetric charge sharing have more chance for survival if these are in highly excited states. It should be noted that the asymmetry in (1, 2) channel is preserved in any case.
For (1, 2) channel, difference in the KER distribution between zero and one Auger emission seems to be small, while that correlated with zero Auger is slightly broader. On the other hand, a clear difference can be seen in (1, 3) channel between the processes with one and two Auger electrons. This is also the case for (1, 4) channel, although the difference is somewhat less clear because of the lower statistics. This propensity can be interpreted by a simple picture based on the classical over-barrier model (COBM). According to the COBM, electron capture at a larger impact parameter leads to production of higher electronic states of the scattered ion (electron acceptor) and lower electronic states of the recoil ion (electron donor). Then the scattered ions in the higher electronic states tend to emit more electrons, and the recoil ions in the lower electronic states tend to give lower KER. These are indeed observed in the present study.

4. Conclusion
The KER distributions for asymmetric fragmentation channels of multiply ionized N\textsubscript{2} were successfully measured for the selected charge states of the scattered ions. The propensities found for KER distributions are qualitatively consistent with a simple picture based on COBM. To find the reason why the (1, 2) channel does not show a clear dependence on the electron capture process, and to explore the generality of this finding, further measurements are needed. So far, we have observed Auger-dependent coulombic dissociation of tri-atomic molecules [6], and plan to study the fragmentation dynamics for more complex molecules [7].

References
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