Fragmentation and desorption in low-energy highly charged ion collisions with molecules and surfaces

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Abstract. In order to study secondary-ion emission in low-energy highly charged ion collisions with molecules and surfaces, we performed coincidence measurements of secondary ions and scattered ions, scattered neutral atoms or secondary electrons. Fragmentation and desorption processes induced by electron captures were successfully extracted by observing the scattered ions/atoms with small scattering angles. Momentum imaging of the secondary ions offers a new analysis method when combined with translational energy spectroscopy or energy-gain spectroscopy of scattered ions. This technique was successful in clarifying the reaction pathways of the electronic transitions of molecules and following the dissociation processes in collisions between Ar$q^+$ ($q = 3–12$) and CF$_4$ and N$_2$ molecules. We also successfully performed secondary ion mass spectroscopy of the topmost layers of the surfaces in glancing collisions between Ar$^{8+}$ and both GaN (0001) and (000$\overline{1}$) surfaces.

1. Introduction
The electron capture cross-section increases almost linearly with an increase in the charge state of incident ions [1]. In addition to a large cross-section that varies with the charge state of ions, the electron capture processes in collisions with highly charged ions (HCIs) have the important characteristic of state selectivity due to their resonant feature called the reaction window [2, 3]. The width of the reaction window is proportional to the collision velocity taking into account the uncertainty, with the barrier height formed in the HCI and target material. The probability of electron capture, especially in low-energy collisions, increases rapidly around a collision energy that matches the binding energy of the electron. On the other hand, fragmentation of molecules and desorption of surface atoms are often induced after electron capture, because the valence electrons corresponding to chemical bonds are captured preferentially by the HCI. In the case of soft collisions, e.g. less correspondence of an interaction with small impact parameters, fragmentation, desorption or sputtering with pure electronic transitions should occur. Soft, state-selective and efficient secondary-particle emission is expected.

To investigate the electronic transitions in HCI–molecule and HCI–surface interactions followed by secondary-particle emissions, time-of-flight mass spectroscopy of secondary ions was performed in coincidence with scattered ions and atoms.

2. Experimental setup and procedures

2.1. Ion–molecule collisions—Coincidence measurements between momentum-imaging spectroscopy of fragment ions and translational-energy spectroscopy of scattered ions
Figure 1 shows a schematic illustration of the experimental setup. This setup [4, 5] makes it possible to perform momentum-imaging spectroscopy (MIS) of secondary ions [6] and translational energy spectroscopy (TES) of scattered ions [7] simultaneously. We observed processes with large impact parameters and small recoil energies by selecting small scattering angles $\theta_i$ ($\theta_i \leq 0.5^\circ$) and small energy gain $Q$ with respect to the incident energy $E_0$ ($Q/E_0 \leq 1 \times 10^{-5}$) [4]. Limited processes without nuclear momentum transfer were observed selectively under these experimental conditions.

The incident energy of Ar$^{q+}$ ($q = 3$–12) was maintained at 8.00 keV. The ions were extracted from an electron beam ion source. The energy gain of the scattered ions was analysed using a $45^\circ$ parallel plate (P3 in Figure 1). The energy resolution of the analyser ($\Delta E/E$) was $2 \times 10^{-4}$. Target molecules were introduced from an effusive nozzle. Note that the nozzle was replaced with the sample holder (H), although it is not illustrated in Figure 1. The red curve in Figure 1 represents a typical HCI trajectory. The flight time $t$ and the position signals $x$ and $y$ of fragment ions hitting the two-dimensional position-sensitive detector (D1) were recorded using a digital oscilloscope triggered by a scattered ion signal of the D2 detector. A three-dimensional (3D) momentum vector of a fragment ion just after electron transfer collision was reconstructed from signals consisting of ($t$, $x$, $y$). The background pressure of the collision chamber was maintained below $2 \times 10^{-6}$ Pa.

2.2. Ion–surface collisions–Coincidence detection between scattered atoms/ions and secondary ions in glancing collisions

A pair of parallel plates (P1 and P2 in Figure 1) was set in front of the target surface to realize glancing collisions without rotating the surface [10–13]. This setup allows us to continue extracting secondary ions along the surface normal direction, even during glancing collisions between the HCIs and surfaces. This is important for the MIS of secondary ions. The angle of incidence $\theta_i$ was controlled by the bias voltage applied to the deflectors. The angle $\theta_i$ is almost independent of the charge state $q$ under a constant acceleration voltage of the HCIs and a constant bias voltage applied to the deflectors. The initial kinetic energy along the surface normal direction, $E_0\sin^2\theta_i$, is very small ($\leq 3.0$ eV) when $E_0 = 2.50 \times q$ keV ($q \leq 14$) and $\theta_i \approx 0.5^\circ$. Kinetic sputtering processes are quite suppressed under this experimental condition. Thus, potential sputtering processes due to electron capture were predominantly observed.

In earlier experiments, coincidence detection was performed between secondary ions and scattered atoms that were completely neutralized at the surface [8–11]. The $45^\circ$ parallel plates (P3) were used to eliminate all scattered ions. The flight time and position signals of secondary ions were also recorded using a digital oscilloscope triggered by a scattered atom signal of the D1 detector.

A novel time-of-flight secondary ion mass spectrometer (TOF-SIMS) and a low-energy scattered ion spectrometer (LEIS) have been developed recently [12]. The kinetic energy and charge state of the scattered ions can be analysed using a Wien filter and the parallel plates, respectively. Coincidence detection between scattered and secondary ions makes it possible to separate potential sputtering from kinetic sputtering.
3. Results and discussion

3.1. Ion-molecule collisions

Figure 2 shows a typical energy gain spectrum of scattered ions (Ar$^{10+}$) in Ar$^{11+}$ + CF$_4$ collisions. The most intense peak labelled S corresponds to a single electron transfer (SET), whereas the three peaks labelled D, T and Q correspond to double (DET), triple (TET) and quadruple electron transfer (QET) processes, respectively, followed by one, two and three Auger electrons. The multiple electron transfer process followed by autoionization is called transfer ionization (TI) [13]. It was found [4, 5] that the $q$-dependence of the energy-gain peaks of each electron transfer process can be fitted with a curve calculated by the classical over-barrier model (COB) [2]. Electron transfer processes can be specified by analysing the energy-gain spectrum.

In the next step, we performed coincidence measurements between the momenta of secondary ions and the energy gains of the scattered ions. Figure 3 shows 3D-momentum images of CF$_3^+$ ions and the kinetic energy released (KER) distribution in collisions of Ar$^{8+}$ + CF$_4$. Each $x$ and $z$ axis in the figure is parallel to the Ar$^{8+}$ beam and TOF axis, respectively. The momentum images of CF$_3^+$ ions were taken in coincidence with those of Ar$^{7+}$ ions having an energy gain of $Q = 15.4$ eV (SET). The entire reaction process, including electron capture and fragmentation, was clarified by the energy balance distributed to the final products (or Ar$^{7+}$, F and CF$_3^+$). The peak KER is 0.28 ± 0.01 eV. This value is in good agreement with those measured by fragment ion-photon coincidence experiments [16, 17]. Thus, the processes were assigned as follows:

$$\text{Ar}^{8+} \left( 2p^6 \, ^1S_0 \right) + \text{CF}_4 \left( \tilde{X} \, ^1A_1 \right) \rightarrow \text{Ar}^{7+} \left( 2p^5 5d \, ^2D_1 \right) + \text{CF}_4^+ \left( \tilde{A} \, ^2T_2 \right) + 15.4 \text{ eV}$$

$$\downarrow \text{CF}_4^+ \left( \tilde{A} \, ^2T_2 \right) + h\nu$$

$$\downarrow \text{F} + \text{CF}_3^+ \quad (1)$$

Some structures seem to appear in the momentum images (a) and (b) of Figure 3. However, further investigation requires more precise measurements. In the case of DET processes, triple coincidence data, e.g. data for a scattered ion, the first and the second arrived fragment ion, were observed, because doubly charged molecular ions produced just after the DET often dissociate into two ionic fragments. Figure 4(a) shows the TOF correlation plot of F$^+$ and CF$_3^+$ ions produced in the DET of Ar$^{8+}$ + CF$_4$ collisions. The horizontal axis is the TOF of the first arrived F$^+$ ion, and the vertical

\[ \text{Counts} \]

\[ \text{Energy gain } Q \text{ (eV)} \]

\[ \text{Counts} \]

\[ \text{KER (eV)} \]

\[ \text{Counts} \]

\[ \text{Counts} \]
axis is that of the second arrived CF$_3^+$ ion [4]. One island around $t_1 \sim 5.1$ µs and $t_2 \sim 10.7$ µs marks ion-pair formation of forwards emitted F$^+$ and backwards emitted CF$_3^+$ with respect to the detector, whereas another island around $t_1 \sim 5.5$ µs and $t_2 \sim 10.3$ µs marks that of backwards emitted F$^+$ and forwards emitted CF$_3^+$. Figure 4(b) and (c) show the momentum images of F$^+$ and CF$_3^+$ ions from the correlation data. Note that each momentum vector was plotted in the centre-of-mass frame of the two fragment ions. The momenta of F$^+$ and CF$_3^+$ ions were clearly separated along the $x$-axis, or Ar$^8^+$ beam axis, as shown in Figure 4(b), although there is almost no anisotropy in $P_x$–$P_y$, as shown in Figure 4(c).

This directly suggests that the CF$_4$ molecule prefers to orient parallel to the HCI-beam direction heading in a fluorine atom in a specific DET-TI process [4], as described below.

$$\text{Ar}^{8+} (2p^6 1S_0) + \text{N}_2 (X^1\Sigma_g^+) \rightarrow \text{Ar}^{6+}^* (2p^6 4f_{5/2}) + \text{N}_2^2+^* (1\Sigma_u^+, 1\Delta_g \text{or } 3\Delta_u)$$

$$\rightarrow \text{Ar}^{7+} (2p^6 3s^2 1I_t) + e^- + \text{N}^+ + \text{N}^+$$

(2)

$$\text{Ar}^{8+} (2p^6 1S_0) + \text{CF}_4 (X^1A_1) \rightarrow \text{Ar}^{6+}^* (2p^6 4f_{5/2}) + \text{CF}_4^{2+^*} (1t_{14^1} 4t_{213^1} 3T_1)$$

$$\rightarrow \text{Ar}^{7+} (2p^6 3s^2 1I_{t/2}) + e^- + \text{F}^+ + \text{CF}_3^+$$

(3)

In the Ar$^{8+}$ + N$_2$ collision experiment, we made sure that there was no significant anisotropy in the $P_x$–$P_y$ momentum images of forwards emitted and backwards emitted N$^+$ ions produced in the same DET process [5]. The physics of this phenomenon are not yet clear, but we can assume that the DET processes in collisions of HCI with CF$_4$ molecules have large cross-sections when an HCI approaches an F atom along the F–C bond. One reason for making this assumption is that according to an evaluation by a simple model calculation based on the COB [2, 16], double electron capture is found to be possible even in the straight-line trajectory with a large impact parameter. However, a more in-depth examination is required.

### 3.2. Ion-surface collisions

We performed coincidence measurements of scattered neutral atoms and secondary ions in the first step. These experiments were performed by applying a high voltage (+3.0–4.0 kV) to the 45° parallel plate to eliminate all scattered ions, as described in 2.2.

Figure 5 shows the momentum image of protons emitted from a GaN(0001) surface interacting with Ar$^{8+}$ at $\theta \sim 0.5^\circ$. This is the first 3D visualization of desorption induced by slow HCIIs having kinetic energy of less than 2.0 eV in the surface normal direction [8]. To measure the charge-state dependence of the proton desorption yield in glancing-angle collisions, we conducted HCI-collision experiments using a polycrystalline aluminium surface. The steady state surface coverage of hydrocarbon molecules was maintained at $\sim 1$ during the experiment, because desorption induced by HCI collisions and adsorption of hydrocarbon molecules were balanced under an HCI flux of $1 \times 10^6$ ions cm$^{-2}$s$^{-1}$ and a residual gas pressure of $1 \times 10^{-7}$ Pa at room temperature [10]. The proton emission...
intensity normalized by the number of incident ions is shown in Figure 6. Note that the intensity is not equal to the sputtering yield, because the detection efficiencies of Ar$^q$ ions, Ar atoms and protons have not been calibrated. It is clear that our experimental data saturates more remarkably than the data that did not include glancing collisions [17]. However, such saturation enhancement was not observed in GaN(0001) or 6H-SiC(0001) surfaces, even in glancing collisions [8]. According to a simple model calculation that includes image acceleration [10, 11], the saturation was clearly enhanced, as shown in Figure 6. Therefore, we conclude that shortening of the interaction time above the surface due to image acceleration of incident ions is one reason for the remarkable saturation of proton emission intensity in glancing collisions with an aluminium surface.

Do substrate atoms emit as secondary ions in glancing collisions? The answer may be yes for semiconducting surfaces, but no for conducting and insulating surfaces. No secondary ions of substrate atoms were found on Al, Cu, Ag, Au and Al$_2$O$_3$ surfaces in coincidence experiments between scattered atoms and secondary ions, whereas Ga$^+$, Si$^+$, N$^+$ and SiC$^+$ were found on GaN and SiC surfaces [8]. These results suggest that the capture of conducting electrons by HCIs induces no secondary ion emission in metal surfaces [18], whereas positive hole charges prevent HCIs from approaching the surface of insulators, i.e. the ‘trampoline effect’ [19].

Here, I would like to show an interesting result of GaN(0001) and (000$\overline{1}$) surfaces. Wurtzite GaN has two lattice polarities of (0001) (Ga face; +c) and (000$\overline{1}$) (N face; −c) [20]. A gallium atom on the topmost layer combines with three nitrogen atoms of the bulk GaN in the (0001) surface, whereas a nitrogen atom on the topmost layer combines with three gallium atoms in the (000$\overline{1}$) surface. TOF-SIMS spectra measured on GaN surfaces with two different lattice polarities are shown in Figure 7. The intensity of Ga$^+$ ions on the (0001) surface was 4.7 times larger than that on the (000$\overline{1}$) surface, whereas the intensity of N$^+$ ions on the (000$\overline{1}$) surface was 1.7 times larger than that on the (0001) surface [9, 11]. This means that the topmost atoms on the Ga or N face were preferentially sputtered. The smaller enhancement factor in the case of N$^+$ may be due to the small probability of ionization by electron capture. This is direct evidence of selective sputtering of the topmost substrate atoms, or SIMS with atomic-depth resolution. This will be a key technique for surface analysis in the near future. More ‘soft’ collisions of HCIs with higher charge state are required for higher selectivity or resolution.

We are developing a novel TOF-SIMS spectrometer combined with a LEIS analyser in order to realize atomic layer–by-layer chemical analysis. We have succeeded in obtaining some preliminary data on proton desorption [12]. Proton emission may be connected in plural kinetic energies of scattered ions in Ar$^{q*}$–GaN(0001) collisions ($\theta \sim 12^\circ$) [21].
4. Summary
To investigate the secondary-ion emissions induced by slow, highly charged ions, time-of-flight mass spectroscopy of secondary ions was performed in coincidence with scattered ions and atoms. This allowed the successful clarification of the dissociation pathways and electronic states of the molecular ions produced just after electron transfer. Selective sputtering of the topmost substrate atoms was observed in GaN single crystals in glancing angle collisions.

It was demonstrated that state- or atomic-layer-specific observation in fragmentation or desorption was possible by observing limited processes with small scattering angle. This fact suggests that both molecules and topmost atoms on surfaces may be excited state-selectively in electron capture processes with HCIs.

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