Energy Redistribution in $I_2^-(CO_2)_n$ Collision on Silicon Surface

Hisato Yasumatsu,[†] Shin'ichi Koizumi,[‡] Akira Terasaki,[†] and Tamotsu Kondow*[,†]

Cluster Research Laboratory, Toyota Technological Institute: East Tokyo Laboratory, Genesis Research Institute, Inc., 717-86 Futamata, Ichikawa, Chiba 272-0001, Japan

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A process of energy redistribution in the collision of $I_2^-(CO_2)_n$ ($n = 1-50$) with a silicon surface was investigated by measuring the surface-parallel translational energy at the collision energy of 50 eV per I_2^- and at the two different angles of incidence, 26° and 45°, with respect to the surface normal. The distributions of the surface-parallel translational energy for all the fragment anions produced from a given parent cluster anion are found to be almost identical in shape and are expressed in terms of a shifted Maxwell−Boltzmann distribution with an effective temperature and a center-of mass translational energy. It is concluded that (1) an incoming parent cluster anion and its neighboring surface atoms reach quasi-equilibrium before its fragment anions leave the surface and (2) a smaller number of surface atoms participate in the energy redistribution at a larger angle of incidence.

1. Introduction

Impact of a cluster onto a solid surface has been investigated, with particular attention on impulsive and coherent interparticle collision occurring in the cluster.[1−37] One of the pioneering works is a computer simulation of $(Ar)_{561}$ collision events onto an NaCl(001) surface by Cleveland and Landman,[1] who have predicted a local and temporal rise of energy and density in the colliding $(Ar)_{561}$. At the collision energy of 2 eV per argon atom, the effective temperature and pressure reach as high as 4000 K and 10 GPa, respectively. It is expected, therefore, that specific chemical reactions that scarcely occur in ordinary chemical environments proceed under such an extreme condition. In fact, Levine et al. have predicted that a four-center reaction having a high activation barrier of ~ 13 eV

$$N_2 + O_2 \rightarrow 2NO \qquad (1)$$

proceeds in a van der Waals cluster, $(N_2{\cdot}O_2)(Rg)_n$ (Rg: rare-gas atom), when the cluster impinges on a solid surface.[11−13]

Experimentally, Vach et al. have studied the collision of large neutral argon clusters onto a pyrolytic graphite surface at collision energies as low as ~ 0.1 eV per argon atom.[25−29] They have concluded that an incoming argon cluster is strongly deformed so that its fringe portion spreads outward very rapidly while its central portion simply evaporates. Evidently, this collision is far from a statistical event as the incoming argon cluster breaks into argon atoms instantaneously when it collides onto the surface. In other words, there is not much chance for the scattered atoms to exchange their kinetic energies before they leave the surface. Raz et al. have reported a phase transition-like phenomenon in a cluster-surface impact; shattering of a cluster to small fragments occurs above a critical collision energy.[4] We have studied[14−19] collision of $X_2^-(CO_2)_n$ ($X = I$, Br, $n \leq 50$) onto a silicon surface at collision energies from 20 to 70 eV per X_2^-. We have concluded that (1) the collision energy is transmitted efficiently to the vibrational mode of the core ion, X_2^-, by a wedge action of CO_2 molecules (*wedge effect*) located at waist positions of the X_2^-,[14−17] (2) the energy deposited in the X_2^- is redistributed among the CO_2 molecules and neighboring surface atoms, and (3) the cluster anion and the surface atoms reach quasi-equilibrium before the fragment anions leave the surface.[18]

In general, a cluster-surface impact proceeds in such a manner that an incoming cluster ion transmits its collision energy to neighboring surface atoms, and then fragments leave the surface after energy redistribution among the cluster and the surface atoms. The energy redistribution changes critically depending on how the energy is transmitted from the translational degree of freedom of the incoming cluster ion to the internal degrees of freedom of the cluster ion and the surface atoms. One can study the energy redistribution by observing energy release in the translational motion of the fragments. As the energy transmission from the incoming cluster ion depends specifically on the direction of the incoming cluster ion, it is useful to acquire information on how the translational energy release depends on the surface-normal and surface-parallel components of the collision energy.

In this connection, we investigated energy redistribution in $I_2^-(CO_2)_n$ through the measurement of the translational energy release in fragment anions from the surface when the cluster anion collides with a silicon surface at different angles of incidence and at a given collision energy. It is found that the number of the surface atoms involved in the collision event decreases with increasing angle of incidence, while the quasi-equilibrium is still valid.

2. Experimental Section

The measurements were performed in a tandem time-of-flight mass spectrometer (TOF-MS) equipped with a cluster ion source and a collision chamber. As the detailed description has been reported previously,[18] this paper gives a brief description related to the present study. Cluster anions were produced by introducing 350-eV electrons into supersonic expansion of a gas mixture of I_2 and CO_2[38] and were accelerated up to 4000 eV. A cluster anion, $I_2^-(CO_2)_n$, with a given n was selected out of a train of

* To whom correspondence should be addressed.
[†] Cluster Research Laboratory, Toyota Technological Institute.
[‡] East Tokyo Laboratory, Genesis Research Institute.

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the spatially separated cluster anions by a mass gate[14,39] in the primary TOF-MS. In the collision chamber evacuated down to 3.5×10^{-8} Pa, the size-selected cluster anion was allowed to collide with a silicon surface placed at the bottom of the reflectron at a given collision energy (per I_2^-), E_{col}, and a given angle of incidence, Θ, with respect to the surface normal direction. Product anions scattered from the surface were mass-analyzed in the secondary TOF-MS and detected by a micro-channel-plate (Hamamatsu F4655 with an effective diameter of 14 mm) mounted on a support that is movable in parallel to the silicon surface. The surface-parallel component of the translational energy, $E_{||}$, (surface-parallel translational energy) of a product anion was measured by changing the position of the detector in parallel to the silicon surface.[18] The detector gain was compensated by assuming that it is proportional to the velocity of the ion detected.[40]

The collision energy (per I_2^-), E_{col}, and the angle of incidence, Θ, were determined by a voltage, V_S, biased at the surface and the angle of the cluster-ion beam axis with respect to the surface-normal direction.[18] In the present study, E_{col} was fixed at 50 eV, and Θ was set at either 26° or 45°. The uncertainties (1 standard deviation) in E_{col} and Θ were typically ± 8 eV and 4°, respectively, in the $I_2^-(CO_2)_{16}$ collision, where a full width at half-maximum (fwhm) of the translational energy of the incident cluster anion was measured to be ~ 30 eV (per cluster anion) irrespective of the cluster size, n. This energy spread is attributed mainly to a spatial distribution of the parent cluster anion at the first stage of the acceleration region in the primary TOF-MS.

The surface-parallel translational energy, $E_{||}$, of a product anion is related to the detector position as

$$E_{||} = qV_S \tan^2 \phi \qquad (1)$$

where q is the electric charge of the product anion and ϕ is the angle of detection with respect to the surface-normal direction.[18]

An n-type Si(100) wafer (specific resistance of ~1000 Ω cm) provided from Toshiba was treated in hydrogen sulfide/hydrogen peroxide aqueous solution, and then in hydrochloric acid/hydrogen peroxide aqueous solution. After the treatment, the thickness of the silicon oxide layer on the silicon wafer was measured to be 1.61 nm by ellipsometry with the refractive index fixed at 1.460. The thickness of the oxide layer would increase by ~10% by oxidation during its transportation in air. A silicon sample (25×15 mm^2) shaped from the wafer was heated at 1000 K by bombarding electrons (350 eV, 100 mA) at the rear side of the surface under the ambient pressure of 2×10^{-7} Pa.[41] By this heat treatment, surface impurities were removed almost completely, but the oxide layer was intentionally left on the silicon surface in order to suppress electron transfer from an incident cluster anion to the surface.

3. Results

Four anions, I^-, $I^-(CO_2)$, I_2^-, and $I_2^-(CO_2)$, were detected in the collision of $I_2^-(CO_2)_n$ ($n \leq 50$). Evidently, I^- and $I^-(CO_2)$ are produced at the collision events in which the core ion, I_2^-, of the parent cluster anion, $I_2^-(CO_2)_n$, is dissociated into I^- and I, and otherwise I_2^- and $I_2^-(CO_2)$ are produced.

Figure 1 shows the distribution of the surface-parallel component of the translational energy (surface-parallel translational energy, $E_{||}$) for the fragment anions produced from $I_2^-(CO_2)_{15}$ at the center-of-mass collision energy (E_{col}) of 50 eV and angles of incidence (Θ) of 26° and 45°. The curves in the figure are described in the Discussion section. The ± signs

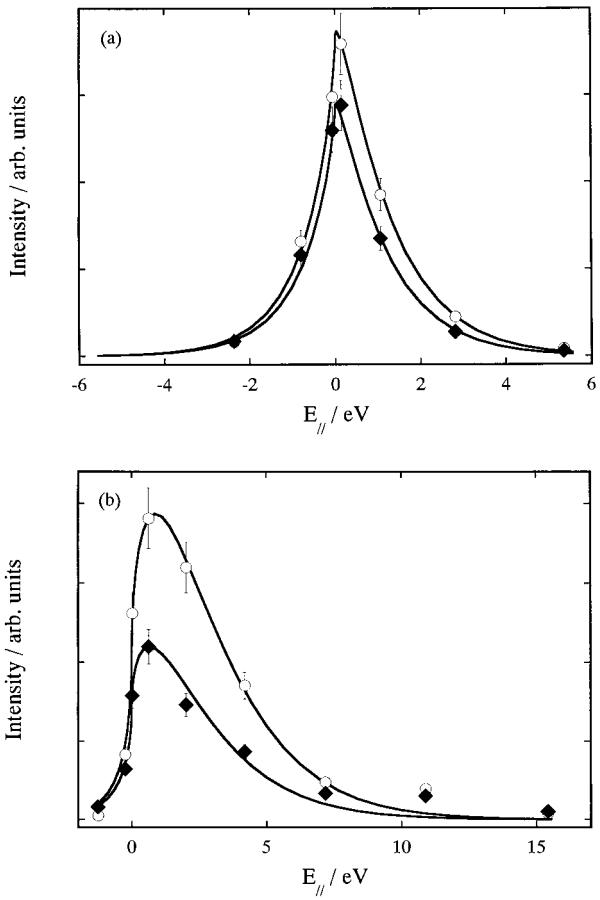

Figure 1. Intensities of the fragment anions, I^- (○) and I_2^-(◆), are plotted as a function of the surface-parallel translational energy, $E_{||}$, in the collision of $I_2^-(CO_2)_{15}$ onto a silicon surface at the collision energy (per I_2^-) of 50 eV and at an angle, Θ, of incidence of (a) 26° and (b) 45° with respect to the surface normal. The solid curves are obtained by least-squares fitting of the $E_{||}$ distributions with a one-dimensional shifted Maxwell−Boltzmann distribution having a translational temperature T_s and a center-of-mass translational energy $E_{||}^{cm}$. For the I^- product anion, $T_s = 10\,800 \pm 1000$ K and $E_{||}^{cm} = 0.01 \pm 0.05$ eV at Θ =26° and $T_s = 15\,500 \pm 1500$ K and $E_{||}^{cm} = 0.8 \pm 0.05$ eV at Θ = 45°. For the I_2^- product anion, $T_s = 15\,500$ K and $E_{||}^{cm} = 0.8$ eV at Θ = 26°, and $T_s = 17\,300$ K and $E_{||}^{cm} = 1.4$ eV at Θ = 45°.

of $E_{||}$ refer to those obtained at the detector positions of $\pm\phi$, respectively. The uncertainties (±10%) of the ion intensities originate mainly from their statistical errors, while those in $E_{||}$ mainly from the systematic error in the determination of the detector position. The essential features of the $E_{||}$ distribution are such that (1) the population decreases exponentially with increasing in $E_{||}$, (2) every fragment anion from a given parent cluster anion has the same $E_{||}$ distribution at any Θ, and (3) the $E_{||}$ distribution measured at Θ = 26 ° has a maximum at $E_{||}$ = 0 eV and is symmetrical with respect to $E_{||}$ = 0 eV, while that measured at Θ = 45 ° has a maximum at $E_{||}$ = 0.5−2 eV in the n range studied.

4. Discussion

A. Quasi-equilibrium Model. In a collision of $I_2^-(CO_2)_n$ on a silicon surface,[18] it has been shown that the incoming cluster ion and its neighboring surface atoms reach a quasi-equilibrium before the fragment ions leave the surface. A major portion of the translational energy (collision energy) of the incoming $I_2^-(CO_2)_n$ is converted to the internal energy of $I_2^-(CO_2)_n$ and the surface atoms involved in the collision event (defined as cluster-surface system); the energy is statistically

redistributed among the internal degrees of freedom of the cluster-surface system. The rest of the collision energy is converted to the translational energy of the center-of-mass of the cluster-surface system.

Let us consider that the cluster anion impinges on the surface with an oblique incidence. A portion of the surface-parallel component of the collision energy is transmitted to the translational energy of the center-of-mass of the cluster-surface system, while the rest is to the internal energy of the cluster-surface system by *friction* between the cluster anion and the surface. On the other hand, the surface-normal component of the collision energy is fully transmitted to the internal energy of the cluster-surface system.

B. Translational Energy Distribution. The $E_{||}$ distribution is then expressed by a one-dimensional shifted Maxwell−Boltzmann distribution[18] with a translational temperature, T_s, and a velocity, $v_{||}^{cm}$, of the center-of-mass of the cluster-surface system as

$$P(v_{||})\,\mathrm{d}v_{||} \propto \exp\left\{-\frac{^1/_2 m(v_{||}-v_{||}^{cm})^2}{k_B T_s}\right\}\mathrm{d}v_{||} \qquad (3)$$

where $P(v_{||})\,\mathrm{d}v_{||}$ is the population of a given fragment anion having a surface-parallel velocity between $v_{||}$ and $v_{||}+\mathrm{d}v_{||}$, m is the mass of the fragment anion, and k_B is the Boltzmann constant. The theoretical $E_{||}$ distribution for a given product anion was calculated with two variable parameters, T_s and $v_{||}^{cm}$, where the effects due to a finite divergence of the incoming cluster-anion beam (7 mm in diameter) and a finite viewing angle of the detector (14 mm in diameter) were convoluted in the distribution.[18] This calculated $E_{||}$ distribution was compared with the experimental one, and the best-fit T_s and $v_{||}^{cm}$ were obtained by using the least-squares fitting procedure. For the product anion, I^-, T_s and $E_{||}^{cm} = {}^1/_2 m(v_{||}^{cm})^2$ values at $\Theta = 26°$ were 10800 ± 1000 K and 0.01 ± 0.05 eV, respectively, and those at $\Theta = 45°$ are 15500 ± 1500 K and 0.8 ± 0.05 eV, respectively. Almost the same values were obtained for the I_2^- product (see caption of Figure 1). The uncertainties in T_s and $E_{||}^{cm}$ arise from statistical errors in the intensities of the fragment anions and systematic errors in the fitting and the determination of the detector position; the uncertainties of T_s and $E_{||}^{cm}$ are determined to be typically 10%.

c. Size-Dependence of Translational Temperature and Energy. Figure 2 shows the dependence of T_s and $E_{||}^{cm}$ on the number, n, of the CO_2 molecules contained in the incoming cluster anion. There is an increasing tendency of T_s and $E_{||}^{cm}$ with n and Θ. In the framework of the quasi-equilibrium model, the fragment anions are considered to evaporate from the cluster-surface system having an effective temperature. Therefore, the translational temperature, T_s, of the fragment anions should be equal to the effective temperature of the cluster-surface system. It follows that the ordinate of Figure 2a (T_s) should be read as the effective temperature of the cluster-surface system.

As explained below, T_s increases linearly with $n^{1/3}$ in the framework of the quasi-equilibrium model: The internal energy increases almost linearly with n at a given collision energy and angle of incidence, because the collision energy per I_2^- is always maintained at 50 eV and is converted almost fully to the internal energy of the cluster-surface system. Let us consider that the incoming cluster anion interacts with surface atoms up to a depth d. Note that d remains unchanged when the collision energy and the angle of incidence are fixed. Then the number of the surface atoms involved in the collision event is approximated by the product of d and the geometrical cross section of the incoming cluster anion, which is proportional to $n^{2/3}$. It turns out that T_s increases linearly with $\sim n^{1/3}$ by taking into consideration that T_s is defined by the energy partitioned by one degree of freedom of the cluster-surface system and d is regarded as a constant.

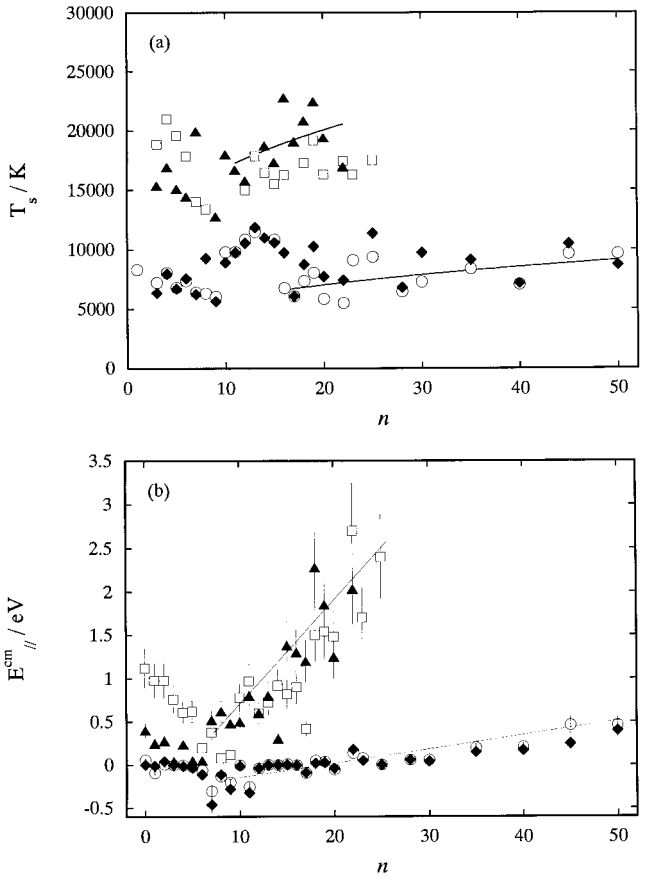

Figure 2. Cluster-size dependence of (a) the temperature, T_s, and (b) the center-of-mass translational energy, $E_{||}^{cm}$, of the fragment anions, I^- and I_2^-, at the collision energy (per I_2^-) of 50 eV and angles of incidence, Θ, of 26° and 45° with respect to the surface normal. The symbols ○ and ◆ represent the values of I^- and I_2^- at $\Theta = 26°$, respectively, and the symbols □ and ▲ represent the values of I^- and I_2^- at $\Theta = 45°$, respectively. The solid curves in panel a exhibit an $n^{1/3}$ dependence, and those in panel b provide eye guides.

On the other hand, the increase of $E_{||}^{cm}$ with n (see Figure 2b) implies that solvent CO_2 molecules behave as lubricant so that the cluster-surface system moves on the surface more readily when more CO_2 molecules are attached to the core ion, I_2^-. The lubrication by the CO_2 molecules may arise from the fact that the interaction between the core ion and a CO_2 molecule is weaker than that between the core ion and the surface.

D. Number of Surfaces Atoms in Cluster-Surface System. In the scheme of the quasi-equilibrium model, the internal energy, E_{int}, of the cluster-surface system is related to the total number of the atoms (n_{tot}) of the cluster-surface system as

$$E_{int} = \frac{1}{2}k_B T_s(3n_{tot}-6)\,E_{col}\frac{2m_I + nm_{CO_2}}{2m_I} - \frac{1}{2}m_{tot}(v_{||}^{cm})^2 \qquad (4)$$

where ${}^1/_2 m_{tot}(v_{||}^{cm})^2$ is the translational energy of the center-of-mass of the cluster-surface system (see eq 3), and m_{tot} is the total mass of the cluster-surface system, which is given by the sum of the masses of an iodine atom (m_I), a CO_2 molecule (m_{CO_2}) and a silicon atom (m_{Si}) as

$$m_{tot} = 2m_I + nm_{CO_2} + (n_{tot} - 2 - 3n)m_{Si} \quad (5)$$

The n_{tot} value is calculated from eqs 4 and 5. Figure 3 shows the n-dependence of n_{tot} at $\Theta = 26°$ and 45°. As shown in section 3C, the total number of the atoms, n_{tot}, increases almost linearly with $\sim n^{2/3}$ irrespective of Θ, as shown by the solid curves in the figure. The validity of the quasi-equilibrium model is again proved by the $n^{2/3}$ dependence of n_{tot}. The number of silicon atoms in the $\Theta = 26°$ collision is 3 times as large as the number of atoms involved in the incident cluster anion, while that in the $\Theta = 45$ ° collision is roughly equal to the number of atoms in the cluster anion. The decrease of n_{tot} with the angle of incidence (see Figure 3) implies that the incoming cluster anion plunges more deeply into the surface at a smaller angle of incidence due to an increasing surface-normal component of the collision energy.

E. Cluster Volume. The effective volume, V, is also estimated at the moment of attaining the quasi-equilibrium between I^- and CO_2 as

$$I^- + nCO_2 \rightleftharpoons I^-(CO_2) + (n-1)\,CO_2 \quad (6)$$

where I^- is a product of surface-impact dissociation of the core ion, I_2^-. As described in our previous paper,[18] the effective volume is given by

$$V = \frac{(f_{I^-(CO_2)} - n)(f_{I^-(CO_2)} - 1)}{f_{I^-(CO_2)}(n - f_{I^-(CO_2)} + 1)} K(n+1)k_B T \quad (7)$$

where K is the equilibrium constant for eq 6 at a given temperature, T, and $f_{I^-(CO_2)}$ is a branching fraction of $I^-(CO_2)$ formation, defined by

$$f_{I^-(CO_2)} = \frac{[I^-(CO_2)]}{[I^-] + [I^-(CO_2)]} \quad (8)$$

where [Y] represents the intensity of Y [Y = I^- or $I^-(CO_2)$]. The volume, V, is estimated by substitution of T with T_s, along with the reported K value.[42] The number density is high as 9×10^{19} cm^{-3} and 2×10^{19} cm^{-3} in the $\Theta = 26°$ and 45° collisions, respectively.

5. Conclusion

The scheme of the collisional dissociation of $I_2^-(CO_2)_n$ by surface impact was elucidated by measuring the surface-parallel translational energy of the fragment anions from the surface at two different angles of incidence. The result shows that the incoming cluster anion reaches quasi-equilibrium with relevant surface atoms before the fragment anions leave the surface. The number of surface atoms involved in the collision event increases with decreasing angle of incidence, since the incoming cluster anion plunges into the surface more deeply due to the increase of the normal translational energy with the decrease of the angle of incidence.

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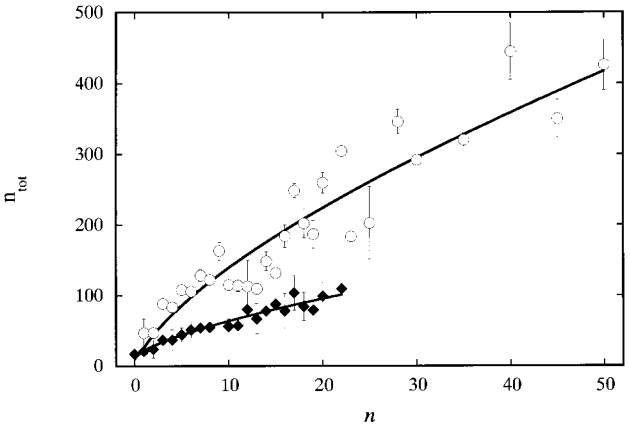

Figure 3. Number of atoms in the incoming cluster anion, $I_2^-(CO_2)_n$, and the relevant surface silicon atoms involved in quasi-equilibrium. The collision energy (per I_2^-) is 50 eV and the angles of incidence are 26° (○) and 45° (◆) with respect to the surface normal. The solid curves exhibit an $n^{2/3}$ dependence.

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