Assistance of Core-Ion Dissociation by Energy Transmission from Solvent Molecules in $N_3O_3^-(NO)_n$ (n = 0–38) Impact onto Silicon Surface

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A size-selected cluster anion, $N_3O_3^-(NO)_n$ (n = 0–38) , was allowed to collide onto a silicon surface, and the product anions, NO_2^-, $N_2O_2^-$ and $N_3O_3^-(NO)_m$ (m = 0–2), from the surface were observed mass-spectroscopically. The branching fractions of the product anions were measured as functions of the energy of the incoming parent cluster anion and the size, n. It was found that NO molecules located in the vicinity of the core ion, $N_3O_3^-$, transmit their kinetic energy to $N_3O_3^-$ most efficiently.

In the collision of a cluster ion onto a solid surface, the kinetic energy of the incoming cluster ion is converted very efficiently to its internal energy,[1–3] especially to that of its core ion. In a surface impact of $I_2^-(CO_2)_n$, the kinetic energy of the solvent CO_2 molecules at the waist positions of the core ion, I_2^-, is transmitted intensively to the I_2^- bond, and as a result, the bond splits as if a piece of wood splits by a hammer thrust against a wedge.[4–6] This finding shows that the energy transmission depends critically on the solvation structure and the number of the solvent molecules.[4–7] It is important to know how much energy is transmitted to the core ion from a solvent molecule of a known location in the solvation structure. This energy transmission is appropriately observed in the collision of $N_3O_3^-(NO)_n$ onto a solid surface through monitoring the branching fractions of the two dissociation channels of the core ion, $N_3O_3^-$, into NO_2^- and $N_2O_2^-$.[8–10] Note that the cluster anion consists of a 'hard' core ion, $N_3O_3^-$, and a 'soft' solvation shell, $(NO)_n$.[11,12] In this connection, we studied the impact of size-selected $N_3O_3^-(NO)_n$ onto a silicon surface.

The measurements were performed in a tandem time-of-flight (TOF) mass spectrometer equipped with a cluster ion source and an ultrahigh-vacuum surface-collision chamber.[4–6] A gas mixture of 5–20% nitric oxide (Nihon Sanso, 97% pure) in argon (Nihon Sanso, 99.9995% pure) having a pressure of 4 atm was passed through a coiled tube cooled in a slush bath of an ethanol/liquid-nitrogen mixture at a temperature of ~170 K; impurities such as nitrogen dioxide and water were eliminated. The gas mixture was expanded supersonically into the source chamber from a pulsed valve. Cluster anions, $N_3O_3^-(NO)_n$, were produced by injecting electrons (50–300 eV) into the supersonic expansion region,[13] and a cluster ion of a desired size was selected by using a mass gate placed in the primary TOF mass spectrometer. The cluster anion, $N_3O_3^-(NO)_n$, with a given n (n = 0–38) was allowed to collide onto a silicon surface at a collision energy, E_{col}, per core ion. The uncertainty in E_{col} was determined by a retarding potential method for every cluster size; typically, 1.8 eV (one-standard deviation) in the collision of $N_3O_3^-(NO)_8$. The product anions from the surface were mass-analyzed in the secondary TOF mass spectrometer. It was found that the detector collects more than 90% of the product anions. All the measurements were performed at a temperature of 300 K and a pressure less than 4×10^{-8} Pa. The silicon surface (25×15 mm^2) was prepared by heating a p-doped Si(100) wafer (specific resistance of 4.5–6 Ω cm) covered with silicon oxide layers (9-nm thickness) at 900 K for 10 hours under an ambient pressure of ~10^{-7} Pa or less.

Upon the impact of $N_3O_3^-(NO)_n$, NO_2^-, $N_2O_2^-$ and $N_3O_3^-(NO)_m$ (m = 0,1,2), together with a trace amount of NO^- and O^-, were scattered from the surface. The branching fractions, f_x (x = 1,2,3), of the product anions, NO_2^-, $N_2O_2^-$ and $N_3O_3^-(NO)_m$, respectively, are given by

$$f_x = \frac{[Y]}{[NO_2^-]+[N_2O_2^-]+\sum_{m=0}^{2}[N_3O_3^-(NO)_m]}, \qquad (1)$$

where [Y] represents the intensity of a given product anion, Y.

The branching fractions, f_x (x = 1,2,3), for the $N_3O_3^-$ impact are plotted against the collision energy, E_{col}, per $N_3O_3^-$ in Figure 1. The branching fraction (f_1) for the NO_2^- production starts to increase in the vicinity of the smallest collision energy studied (~6 eV); the appearance energy of NO_2^- is determined to be 6 ± 8 eV. Note that NO_2^- is produced from $N_3O_3^-$ specifically in the surface impact probably because of impulsive energy transmission to the internal modes of $N_3O_3^-$. On the other hand, the

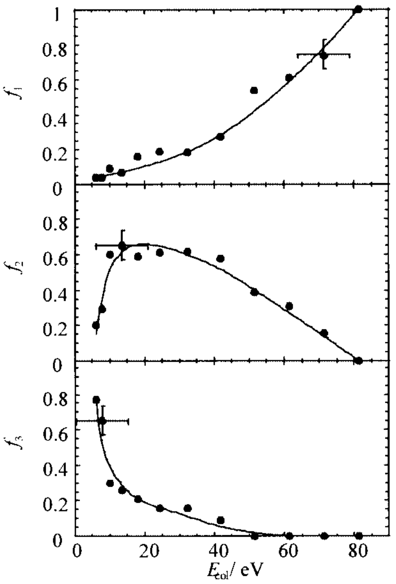

Figure 1. Branching fractions, f_1, f_2 and f_3, for the production of NO_2^-, $N_2O_2^-$ and $N_3O_3^-$, respectively, as a function of the collision energy, E_{col}, in the impact of $N_3O_3^-$. The solid curves represent eye guides. The definition of the branching fractions is given in text.

branching fraction (f_2) for the $N_2O_2^-$ production rises sharply at the smallest collision energy studied. This finding is consistent with the barrier height of less than 2.5 eV[8] for the reaction,

$$N_3O_3^- \rightarrow N_2O_2^- + NO. \qquad (2)$$

Figure 2 shows f_1 and f_2 as a function of the collision energy, E_{col}, when $N_3O_3^-(NO)_n$ is allowed to collide onto the silicon surface. A reaction mechanism similar to that for the $N_3O_3^-$ impact is operative because $N_3O_3^-(NO)_n$ consists of a hard core ion, $N_3O_3^-$, and a soft solvation shell, $(NO)_n$,[11,12] that is, $N_3O_3^-$ dissociates by the surface impact with the assistance of kinetic-energy transmission from NO molecules in the shell. Actually, a less collision energy is needed to obtain the same f_1 and f_2 values if the core ion possesses a more number of NO molecules (see Figure 2). In other words, the core ion, $N_3O_3^-$, gains an effective collision energy, E_{eff}; the sum of prompt energy gain by surface collision of the parent cluster anion and subsequent energy gain, E_{solv}, through intracluster collision with the solvent NO molecules. The prompt energy gain is given by the collision energy, E_{col}. The effective collision energy is then expressed as

$$E_{eff} = E_{col} + E_{solv}. \qquad (3)$$

As the same reaction mechanism is operative, irrespective of the number of the solvent NO molecules as described above, the dependences of f_1 and f_2 on E_{eff} must be expressed by a universal relationship between f_x (x = 1, 2) and E_{eff} valid at any number of the solvent NO molecules.

Let us define the efficiency of the energy transmission as

$$\eta = E_{solv} / E_{col}. \qquad (4)$$

Then, E_{eff} is given from equations (3) and (4) as

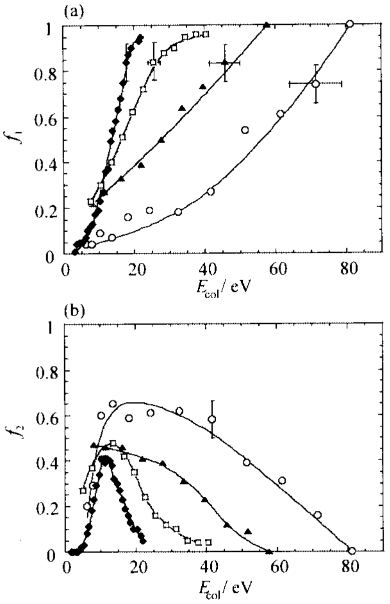

Figure 2. Branching fractions, f_1 and f_2, for the production of NO_2^- (panel a) and $N_2O_2^-$ (panel b) from $N_3O_3^-(NO)_n$ as a function of the collision energy, E_{col}, (per core ion, $N_3O_3^-$). The marks, ○, ▲, □ and ◆, show the branching fractions for n = 0, 2, 7 and 38, respectively. The solid curves represent eye guides. The definition of the branching fractions is given in text.

$$E_{eff} = E_{col}(\eta + 1). \qquad (5)$$

The efficiency, η, is determined so that the dependences of f_1 and f_2 on E_{eff} are expressed by the universal relationship. As η is zero for the $N_3O_3^-$ impact or for n = 0, the universal relationship coincides with that for the $N_3O_3^-$ impact. Figure 3 shows the η value plotted against the number of the solvent NO molecules. The η values obtained from the f_1–E_{col} and f_2–E_{col} relations coincide. The steep slope in the $n < \sim 8$ range and the gentle slope in the $n > \sim 10$ range indicate that NO molecules in the vicinity of the core ion transmit their kinetic energy much more efficiently than those apart from the core ion. The slope of the η–n plot in the $n < \sim 8$ range (see Figure 3) shows that the effective collision energy of the core ion (E_{eff}) increases by 25% per one NO molecule located in the close vicinity of the core ion. The f_2–E_{col} relation at energies lower than ~10 eV was ruled out because NO release from a parent cluster anion dominates in this energy range.

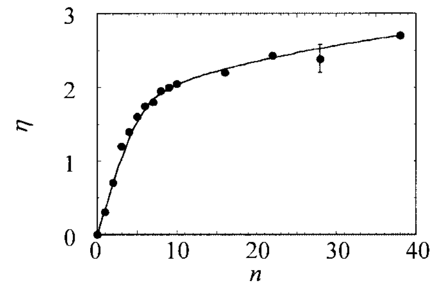

Figure 3. Efficiency, η, for energy transmission from the solvent NO molecules to the core ion, $N_3O_3^-$, as a function of the number of the solvent NO molecules, n. The solid curve represents an eye guide. The definition of η is given in text.

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