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Molecular Dynamics Simulation of Dynamic Solvation Effect in the Collision of $I_2^-(CO_2)_n$ Cluster with Si Surface

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Cluster-surface collision induced dissociation of an I_2^- molecule initially embedded in a $I_2^-(CO_2)_n$ cluster was investigated. Molecular dynamics simulation which provides a microscopic description for energy acquisition in the cluster-surface impact. The trajectory calculations using a realistic Si surface model indicate that the collisions of $I_2^-(CO_2)_n$ with a Si surface can be treated as perfectly elastic ones. The dissociation probability of I_2^- was computed for $I_2^-(CO_2)_n$ with n=0-6 on the basis of a hard-wall model. The size dependence of the dissociation probability ascribable to the wedge effect by a CO_2 molecule located halfway between the I atoms, which is consistent with experimental result by Yasumatsu et al.

KEYWORDS: cluster-surface collision, molecular-dynamics simulation, solvation effect, Si potential

1. Introduction

By high-energy cluster-wall collisions, an extremely high transient particle density, temperature, and energy density can be temporarily generated within the cluster on the femtosecond time scale. The cluster constitutes a new medium, in which novel processes of energy acquisition and disposal are expected to occur[1]. From the theoretical point of view, approximate model calculations based on the equation of molecular dynamics simulations of high-energy collisions of rare-gas clusters with surfaces were used to provide a microscopic description of the intracluster shock-wave and of energy acquisition processes[2].

Recently, $I_2^-(CO_2)_n$ cluster has been the focus of the photodissociation and recombination study by Lineberger and co-workers[3]. On the other hand, the structural property for $I_2^-(CO_2)_n$ cluster has been investigated by using a molecular dynamics calculation[4,5]. Yasumatsu et al. have investigated the collisional processes of $I_2^-(CO_2)_n$ clusters with a silicon surface and found that the dissociation probability of I_2^- depends characteristically on the number of the solvent CO_2 molecule[6]. In this study, the molecular dynamics simulation of $I_2^-(CO_2)_n$ cluster - silicon surface impact has been performed, for the purpose of understanding the size-dependent dissociation probability on the basis of a microscopic collisional process.

2. Methodology and Discussion

A. $I_2^-(CO_2)_n$ potential model

The potential energy function of $I_2^-(CO_2)_n$ is comprised of intramolecule and intermolecule potentials. The I_2^- intramolecular potential is represented by a Morse potential with the parameters D_e=1.10 eV, r_e=3.23 Å and β=1.16 Å^{-1}. The CO_2 intramolecule potential is written by

$$V_{CO_2} = \frac{1}{2}k(r_1 - r_e)^2 + \frac{1}{2}k(r_2 - r_e)^2 + h(\Delta\alpha)^2,$$

where, k=15.5 md/Å and h=0.57 md/Å.

The $I_2^-(CO_2)_n$ intermolecular potential is assembled from the van der Waals and electrostatic interactions induced by excess charge of the I_2^- core ion. The van der Waals interactions are described by Lenard-Jones pair potentials. Lenard-Jones centers are located at each atoms of I_2 and CO_2. The potential parameters are

$\varepsilon_{I\text{-}C} = 9.14\times10^{-3}$ eV, $\sigma_{I\text{-}C} = 3.711$ Å,
$\varepsilon_{I\text{-}O} = 1.002\times10^{-2}$ eV, $\sigma_{I\text{-}O} = 3.524$ Å,
$\varepsilon_{C\text{-}C} = 2.256\times10^{-3}$ eV, $\sigma_{C\text{-}C} = 2.824$ Å,
$\varepsilon_{O\text{-}O} = 6.477\times10^{-3}$ eV, $\sigma_{O\text{-}O} = 3.026$ Å,
$\varepsilon_{C\text{-}O} = (\varepsilon_{C\text{-}C}\,\varepsilon_{O\text{-}O})^{1/2}$, $\sigma_{C\text{-}O} = (\sigma_{C\text{-}C} + \sigma_{O\text{-}O})/2$.

The electrostatic interaction consists of the charge-induced dipole interaction and charge-quadrupole interaction between an excess charge and CO_2, and the induced dipole-induced dipole interactions among CO_2

molecules. A point quadrupole of CO_2 is supplemented at the carbon. The quadrupole moment of a CO_2 molecule is -3.66 Debye•Å. Polarizability of CO_2 is 41.0×10^{-25} cm^3 in the direction along the molecular axis and 19.3×10^{-25} cm^3 in the direction normal to the molecular axis.

If we are concerned with charge-induced interactions for I_2^- near its equilibrium configuration, the excess charge can be taken as one half an electronic charge on each iodine atom. However, we treat the dissociation behavior and therefore need to consider the transition from the equilibrium geometry to separated atom/ion limit: $I_2^- \rightarrow I+I^-$. We use a simple switching function proposed by L. Perera and F. G. Amar to describe the charge redistribution on I_2^- with bondlength as[7]:

$$q_{1,2}(r) = -q_{1/2}(1 \pm 1/2\{1+\tanh[\eta(r-\rho)]\}),$$

where ρ and η are assumed to be 4.5 Å and 6.0 $Å^{-1}$, respectively. The plus and minus signs correspond to the formation of the anion and the neutral. We determined randomly which iodine atom takes excess charge in the dissociation.

B. Si surface potential and dynamics

In the tetrahedral semiconductors, such as Si and Ge, no reasonable pair potential will stabilize the diamond structure of the crystal and a multi-body interaction is necessary to represent the potential of the crystal. In the present work, we use the potential constructed by F. H. Stillinger and T. A. Weber (SW potential)[8]. This potential-energy function is resolved into two-body and three-body contributions as follows,

$$V = \sum_{i<}\sum_{j} V_2(r_{ij}) + \sum_{i<}\sum_{j<}\sum_{k} V_3(\vec{r}_i,\vec{r}_j,\vec{r}_k),$$

with the two-body potential, V_2, and the three-body potential, V_3 written by the energy and the length units ε and σ, respectively, as

$$V_2(r_{ij}) = \varepsilon f_2(r_{ij}/\sigma),$$

and

$$V_3(\vec{r}_i,\vec{r}_j,\vec{r}_k) = \varepsilon g(\vec{r}_i/\sigma,\vec{r}_j/\sigma,\vec{r}_k/\sigma),$$

where $\varepsilon=3.4723\times10^{-19}$ J and σ=2.0951 Å. In addition, f represents a function only dependent on a scalar distance as,

$$f(x) = \begin{cases} A\left(\frac{B}{x^p}-1\right)\exp\left(\frac{1}{x-a}\right) & x<a \\ 0 & x \geq a \end{cases},$$

where A=7.049556, B=0.6022246, p=4, and a=1.8. The function g must possess full translational and rotational symmetry:

$$g(\vec{x}_i,\vec{x}_j,\vec{x}_k) = h(x_{ij},x_{ik},\theta_{jik}) + h(x_{ji},x_{jk},\theta_{ijk}) + h(x_{ki},x_{kj},\theta_{ikj}),$$

where θ_{jik} is the angle between r_i and r_k subtended at vertex i, etc. The function, h, has following form:

$$h(x_{ij},x_{ik},\theta_{jik}) = \begin{cases} \lambda\exp\left(\frac{\gamma}{x_{ij}-a}+\frac{\gamma}{x_{ik}-a}\right)\left(\cos\theta_{jik}+\frac{1}{3}\right)^2 & x_{ij}<a \text{ and } x_{ik}<a \\ 0 & x_{ij}\geq a \text{ or } x_{ik}\geq a \end{cases},$$

where λ=21.0 and γ=1.2. Obviously, SW potential is able to stabilize tetrahedral structure.

Interaction potentials between the constituent particles of the cluster and the surface is assumed to be given by the soft-core repulsive potential,

$$\phi = \varepsilon\left(\frac{\sigma}{r}\right)^n,$$

where the parameters, ε and n, are tentatively set to 9 and 7, respectively.

The relative coordinates of CO_2 to I_2 are initially set as given in the literature, keeping $r(I_2\text{-}CO_2)$ =3,527 Å[4,5]. At the beginning of each run, the distance between the center of mass of the I_2^- and the Si surface is 10 Å and other two coordinates parallel to the surface are randomly positioned in the square of a lattice constant. The cluster is initially oriented at given Euler angles with respect to the surface, the angles are given randomly. The center of the mass velocities of the cluster is determined so that the perpendicular and parallel components of the initial kinetic energy of $I_2^-(CO_2)_n$ per I_2^- are 50 eV and 5 eV[6].

The trajectory calculations are carried out by using a fifth-order predictor-corrector procedure with a time step of 0.01 fs. Snapshots of the collision of $I_2^-(CO_2)$, with the Si surface are shown in fig. 1, which displays the wedge effect. At t=0, $I_2^-CO_2$ is located at 10 Å apart from the surface and CO_2 is placed at the side of the Si surface. At t=130 fs, the CO_2 splits into I_2^- and resultingly, the nuclear distance of I_2^- is lengthened. At t=250 fs, the fragmented I and I^- fly toward different directions.

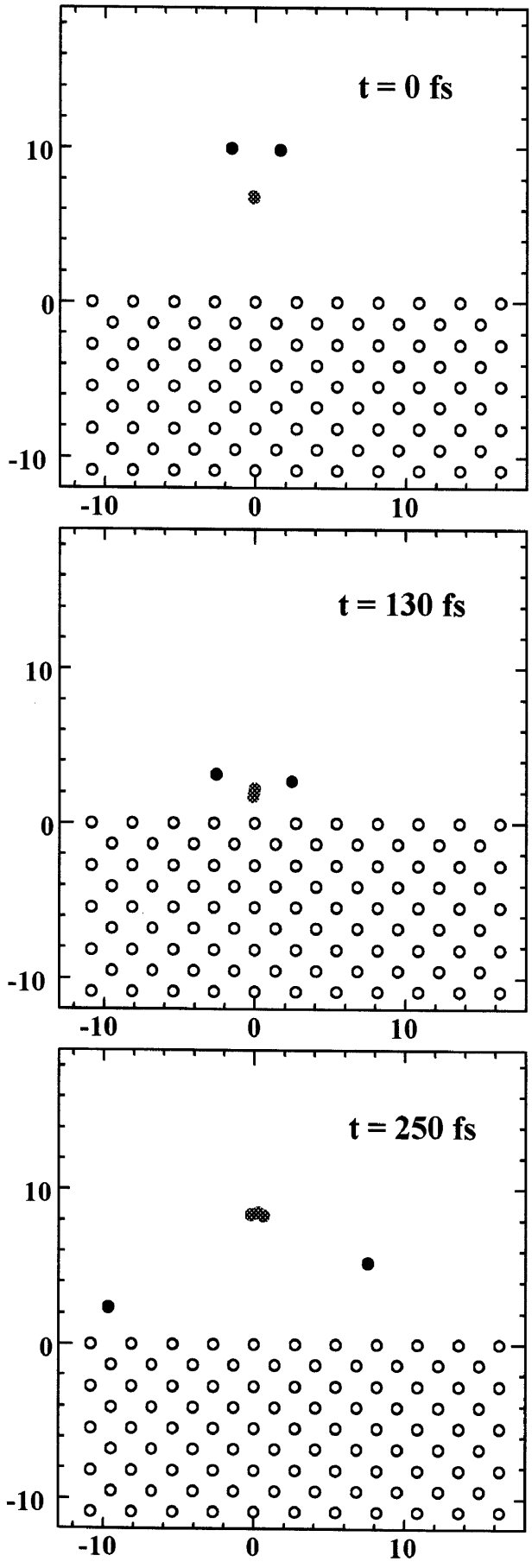

Fig. 1. Snapshots of $I_2^-CO_2$ cluster - Si surface collision. Black, gray, and empty circle represents an I atom, a CO_2 molecule and a Si atom, respectively.

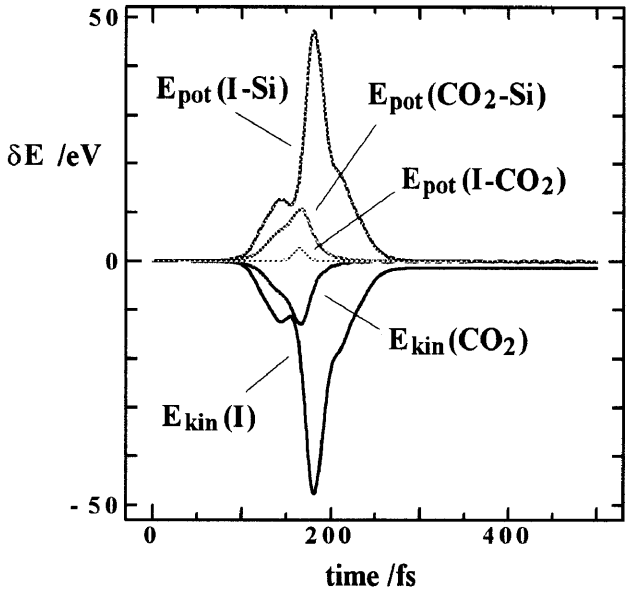

Fig. 2. Time evolution of variation in the cluster energy.

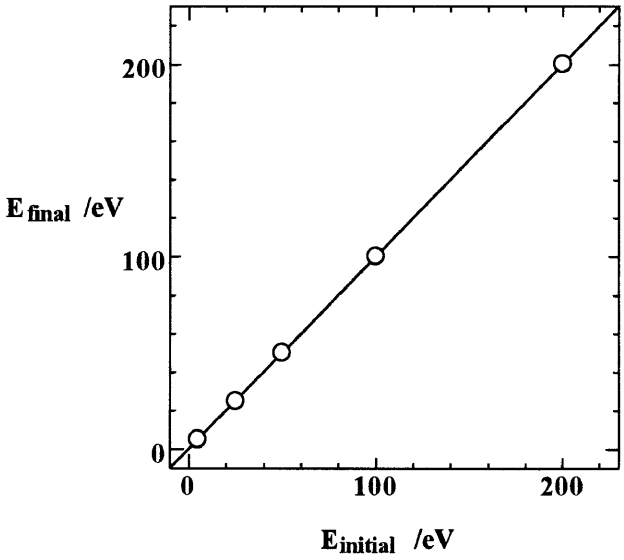

Fig. 3. Final kinetic energy of the I atoms scattered from a realistic Si surface vs the initial kinetic energy. The solid line represents the best fit prediction by a least-squares fitting.

Figure 2 depicts a time evolution of the total energy of $I_2^-(CO_2)_2$ colliding with the Si surface. This result reveals that (1) at impact, kinetic energies of cluster entities almost converted into the potential energies between cluster entities and Si surface, except that a little part converted into potential energy between I and CO_2. (2) after a long time is elapsed, the kinetic energy of I and CO_2 is almost conserved. (3) the energy transferred to Si surface is negligibly small. These behaviors indicate that $I_2^-(CO_2)_n$- Si surface impact can be regarded as an elastic collision.

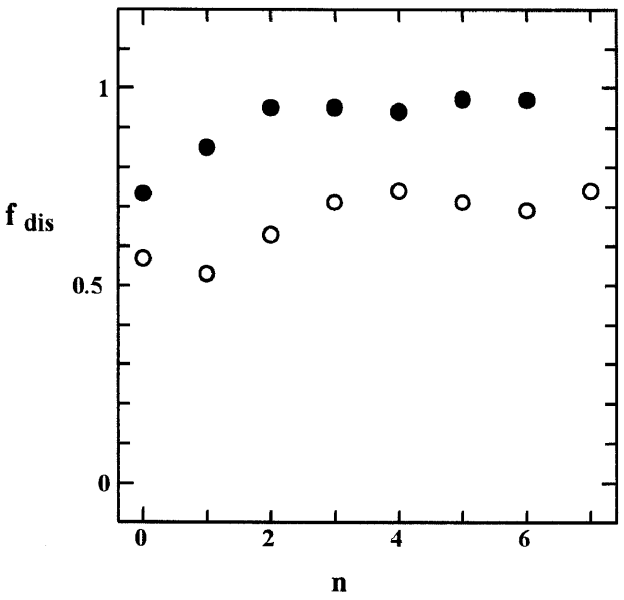

Fig. 4. Dissociation probability of the I_2^- dissociation is plotted against the number of CO_2 molecule, n.
●: calculation given in the present study, and
○: the experimental result [6].

In order to determine the energy range where the $I_2^-(CO_2)_n$-Si surface collision can be regarded as an elastic one, the energy dependence of the restitution coefficient in this collision is calculated. The trajectory of single I atom with a given initial velocity in the direction perpendicular to the surface is computed on the basis of the SW potential. The final kinetic energy of the I atoms scattered from the surface is given as a function of the initial kinetic energy in fig. 3. In the energy range, 10-200 eV, the initial kinetic energy is perfectly conserved, so that the collision with the Si surface can be regarded to be perfectly elastic.

C. Dissociation probability of I_2^-

The simplest model to implement a perfect elastic collisional condition is a hard-wall model, which the component of the velocity perpendicular to the surface is reversed with the other two components remaining the same, upon impact. The molecular dynamics simulations are performed on the basis of this model. The integration time step is Δt=1 fs. The number of CO_2, n, varies from 0 to 6. The trajectories are calculated with 1000 different initial cluster orientations. The dissociation probability of I_2^- increases in the $0 \leq n \leq 2$ range as shown in fig. 4. In this size range, CO_2 is located halfway between the two I atoms[4,5]. In this geometry, the probability of the I_2^- dissociation is enhanced by the wedge effect. In the size range of n=3-6, the dissociation probability is not dependent on n. These size dependencies are consistent with the experimental results[6].

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