MOLECULAR DYNAMICS STUDY OF XE-GRAPHITE (0001) SURFACE SCATTERING

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Abstract. We have investigated the scattering of a hyperthermal Xe from a graphite (0001) surface using the Molecular Dynamics simulations. The angular and velocity distributions of scattered Xe atoms were obtained at incidence energies from 0.45 to 3.5 eV, three incidence angles of 15°, 35° and 60° and the surface temperatures of 300 K and 550 K. The angle-resolved energy ratios of the mean final translational energy over the mean incidence energy E_f/E_i indicate that the Hard-Cube model is applied to this collision system. The weak interplanar potential of graphite disperses the deformation over the wide range of a graphene sheet. Therefore the momentum in the surface normal direction exhibits a large change contrary to the surface tangential momentum. The graphene sheet moves like a trampoline net and the Xe atom like a trampoliner.

INTRODUCTION

The molecular beam scattering experiment under the ultra-high vacuum condition is a very effective tool to obtain a lot of valuable information over the gas-solid surface interaction. Information on a gas-surface potential energy surface and energy transfer mechanisms are important for understanding chemical or physical phenomena. A variety of molecular beam experiments have been performed for a long time. However gas-surface interaction for rare gas atom and a noble metals [1, 2, 3, 4] have been the major topics. Only few investigations have been conducted on the scattering system with heavier gas atoms impinging on lighter surface atoms.

It is still difficult to clarify the detailed dynamics from the molecular beam scattering experiment alone for a heavy projectile incident upon a surface. The numerical analyses of experimental data, however, enable us to extract the essence of the collision events in ideal conditions and to know the mechanism in detail.

We have reported the non-reactive scattering of a massive Xe atom from a graphite (0001) surface using a molecular beam-surface scattering technique and molecular dynamics (MD) simulations [5, 6]. Någård *et al.* [7] also reported the experimental and numerical analyses of Xe scattered from the graphite surface for a wide range of incidence conditions. However their numerical results were obtained for a single incident energy condition and the effect of the velocity distribution of the incident molecular beam was neglected. Their graphite potential model have given a little too high an interplanar debye temperature. Also in the experiment of Någård et al. the distance from a sample surface to a detector was too short to determine the reliable translational energies of the scattered atoms. Thus less information was available in the heavy atom hyperthermal scattering regime. In order to derive a more detailed understanding of the Xe-graphite interaction at hyperthermal incidence energies, the Xe-graphite surface scattering experiments and numerical simulations have been conducted. We have found that the Hard-Cube model [8] which assumes that the momentum parallel to the surface is conserved in the collision process can be approximately applied for the Xe atom-graphite surface scattering, and the numerical results showed very good agreement with the experimental results in both the angle-resolved flux distributions and energy ratios of the incident and scattered gas atom.

To investigate and clarify the mechanism of these phenomena in detail, the Molecular Dynamics (MD) method was adopted to analyze the Xe-graphite gas-surface interaction.

METHOD

The MD method was employed to simulate the scattering of a Xe atom from a graphite surface [9]. All atoms were treated as classical particles. The trajectories of the gas atom and the surface atoms were calculated solving the Newton's equations of motions with the leap-frog method, where the time step was set to $\Delta t = 0.5$ fs.

The potential models used for the graphite intraplanar C-C interactions was based on the empirical potential energy surface by Brenner [10]. The potential parameters for the Brenner potential model was set to the parameterization II in Ref. [10], which gives better stretching force constants. A site-to-site Lennard-Jones (12-6) potential was employed for interplanar C-C pairs with parameters of $\varepsilon = 2.40$ meV, $\sigma = 3.37$ Å. The Lennard-Jones interplanar C-C potential represented the weak van der Waals force between graphene layers. This interplanar potential model gives the Debye temperature of the graphite as $\theta_{D,z} \simeq 1080$ K. The potential model was quite similar to that employed by Någård *et al.* [7] However, the Debye temperature they obtained was somewhat smaller than ours.

The Xe-graphite interaction potential energy surface is represented by a site-to-site Lennard-Jones (12-6) potential between the Xe atom and a C atom in the graphite. The potential parameters were obtained to reproduce the physical adsorption parameters between a Xe atom and a graphite surface: the potential well depth of $D = 132.1$ meV and the equilibrium distance of $z_m = 3.34$ Å[11]. Figure 1 shows a contour plot of the static potential energy surface for two directions using this potential model.

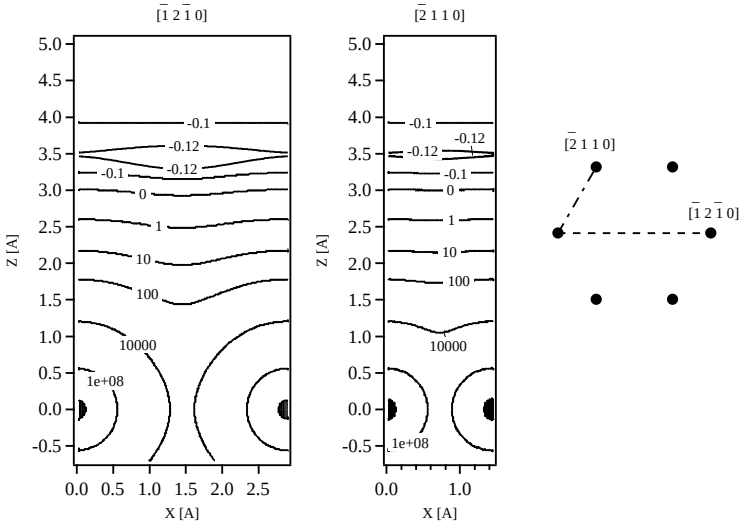

FIGURE 1. Contour plots of the Xe-Graphite (0001) potential energy surface of cross-sectional view normal to the surface along dashed line (left) and chain line (right): the contour values are in electron volts.

As the graphite surface, six layers of 384 carbon atoms with the Miller index of the surface at (0001) were considered using the periodic boundary condition. This was about the size of 30 Å$\times$ 35 Å. Before starting calculations of gas-surface interaction, a thin film of graphite layers was prepared with a two-step scheme; first, under temperature control for 50 000 steps by the velocity scaling technique, and after that 50 000 steps without temperature control to achieve thermal equilibrium. The surface temperature T_s was 300 K or 550 K following the experimental conditions.

A velocity of the incident beam was stochastically given so a velocity distribution of the incident Xe atom in our MD simulations agrees with that obtained from the experimental TOF spectrum, while Någård *et al.* used single incidence energy. The incidence kinetic energy of Xe atoms was set to 0.45, 1.56 and 3.62 eV, and the incidence angle θ_i was 35°. The simulation was continued for 2 000 000 steps, or until the gas atom escaped from the surface. If the total energy of the gas atom was less than $-2kT_s$, the atom was defined as being trapped on the surface. After each collision, the solid surface was set back to the initial condition. For each incidence condition, 10 000 trajectories with random initial position were calculated.

RESULTS AND DISCUSSIONS

Angular and Energy Ratio Distributions

We have simulated Xe atom-graphite(0001) surface scattering process, and compared the results with the experiment and the Hard-Cube model. The Hard-Cube model [8] is the simple model asssuming that the tangential momentum component of the gas atom is conserved during collision. The normal momentum component is altered via an impulsive hard wall collsion with a surface cube vibrating with the surface temperature.

Figure 2 (a)–(c) show the angular flux distributions for $T_s = 550$ K, $\theta_i = 35^\circ$, $E_i = 0.45$, 1.56, and 3.62 eV. The numerical results show good agreement with the experimental results. The larger E_i becomes, the narrower the distribution becomes. And the peak angle of the distribution slightly shifts and converges to the angle $\theta_f = 60^\circ$. The narrowing of the angular flux distributions with increasing incident energy is qualitatively consistent with the prediction of the Hard-Cube model.

The energy ratios of final translational energy to the initial (E_f/E_i) from experiment and simulation are plotted in Fig. 2 (d)–(f) as a function of the scattering angle θ_f. The error bars show the standard deviations of the distributions. The energy distributions exhibit the tendency of the experimental results, whereas the simulation results show a little smaller value compared to the experimental ones. This is because of the dynamic corrugation of the graphite surface and the small intensity of the flux. And it becomes clear that both the experimental and the numerical energy ratios show good agreement with that of the Hard-Cube model.

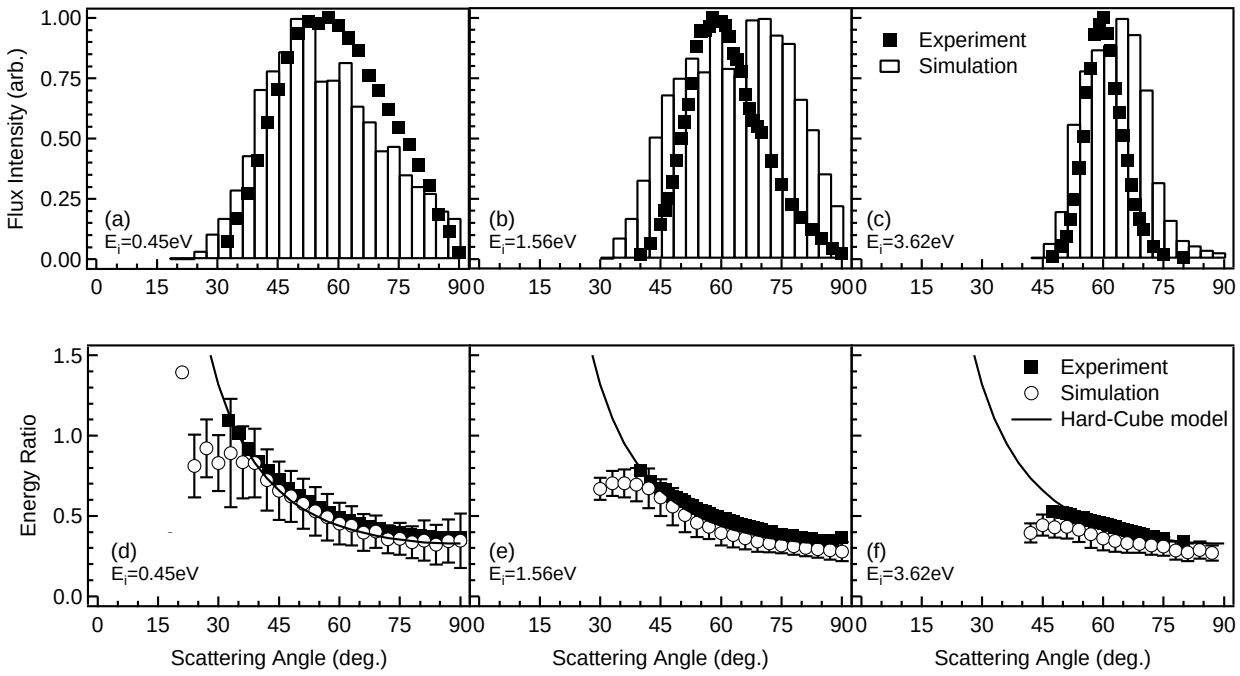

FIGURE 2. Comparison of molecular dynamics results with experiment for $T_s = 550$ K, $\theta_i = 35^\circ$, $E_i = 0.45$ eV (a,d), and 1.56 eV (b,e), and 3.62 eV (c,f). (a)–(c) : the angle resolved flux distributions of scattered Xe atoms, (d)–(f) : the angle resolved energy ratios; ■ : experiment, □ : simulation, solid line : the Hard-Cube model.

Tangential Momentum Conservation

The angle-dependent energy ratios indicate that the Hard-Cube model [8] works for the Xe scattering from a graphite surface. From Fig.1, one sees that the incident Xe atom feels a quite flat graphite surface. The trapping of the incident Xe atom on the graphite surface was rather rare, because of the shallow potential well. Therefore it is reasonable that the tangential velocity component of the incident gas atom is conserved during the collision process, i.e. the tangential velocities of the incident gas atom equals that of the scattered $u_{t,i} = u_{t,f}$. In terms of the incidence angle θ_i and the scattered angle θ_f, the normal velocity component of the incident $u_{n,i}$ and scattered gas atom $u_{n,f}$ are expressed as follows.

$$\begin{aligned} u_{n,i} &= u_{t,i} \cot\theta_i \\ u_{n,f} &= u_{t,f} \cot\theta_f \end{aligned}$$

Therefore the ratio of the normal velocity component was obtained as

$$\frac{u_{n,f}}{u_{n,i}} = \frac{\cot\theta_f}{\cot\theta_i}$$

The angle-dependent momentum ratio of tangential and normal component can be obtained from the simulations. To investigate the effect of the momentum conservation, simulation results are compared with the Hard-Cube model. The ratio of the momentum before to after collision, which is equivalent to the velocity ratio (u_f/u_i) is plotted in Fig. 3. The error bars show the standard deviations of the distributions.

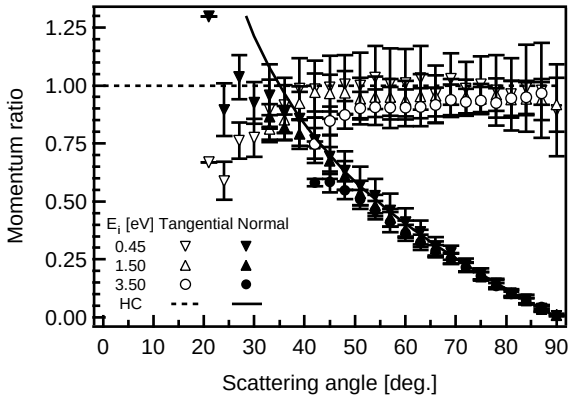

FIGURE 3. Momentum ratio (u_f/u_i) profiles for Xe atoms scattered from the graphite (0001): The incidence kinetic energies in eV are 0.45 (▽), 1.56 (△), 3.62 (○) for tangential components and 0.45 (▼), 1.56 (▲), 3.62 (●) for normal components. The dashed and solid lines (HC) are obtained from the Hard-Cube model for tangential and normal components, respectively.

From this figure, compared to the tangential component, the normal component of the velocity ratio shows quite small deviation. This is because the normal direction of the scattering system can be represented as the flat surface suspended by the "weak" van der Waals force. On the other hand, the tangential component can be affected by the dynamic corrugation of the graphite surface. The deviation of the energy ratio between the numerical results and the Hard-Cube model in the small scattering angle region should be mainly from the dynamic corrugation of the graphite surface and the small intensity of the scattered mass flux.

The information on velocity ratio is important for obtaining the interaction potential energy surface. It is because scattered molecules show the effect of the corrugation of the potential energy surface. Thus the graphite can be represented as a flat surface on the Xe atom impingement at hyperthermal incidence energy.

In the Hard-Cube model, there is no effect of the surface temperature in the energy ratio expression. Therefore we also compared the velocity ratio (u_f/u_i) in two surface temperature conditions $T_s = 300$ K and 550 K, and obtained very good agreement with each other.

Trampoline Motions

The van der Waals radius of Xe (2.18 Å) is larger than the bond length (1.42 Å) for a strong sp^2 C-C bond in the graphite sheet. When a heavy Xe (131 u) impinges upon the surface at high incidence energies, some C atoms feel its impact along the trajectory of the collision event. The Xe atom cannot penetrate deeply into the repulsive part of the interaction potential. Therefore the results of Xe-graphite scattering do not exhibit the effect of the surface corrugation. Owing to strong chemical C-C interaction in each layer of the graphite, many C atoms move at the same time as a sheet. Therefore large deformation of the C atom assembly in graphte occurs as a sheet. One may say that the graphite surface consisting of about 26 C atoms deforms like a "trampoline" net and the Xe atom behaves like a trampoliner.

A trampoline absorbs the normal momentum component of a trampoliner with the large deformation itself. The ratio of the normal momentum component before and after collision is governed not by the incidence conditions, but by the graphite interlayer potential feature.

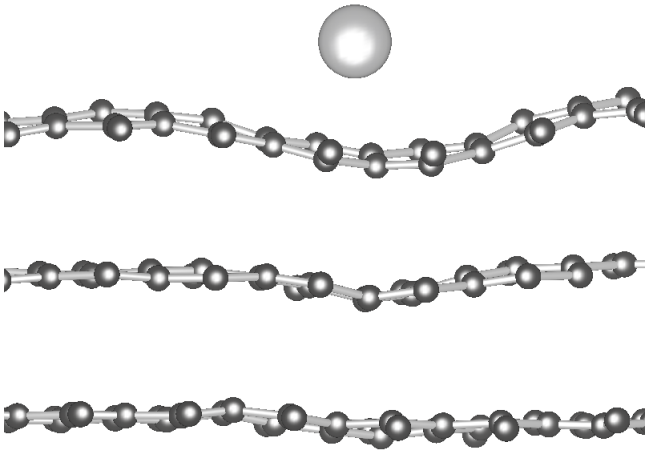

FIGURE 4. A snapshot of the cross section of the trampoline deformations motions from the MD simulation. ($T_s = 550$ K, $\theta_i = 35^\circ$, and $E_i = 3.5$ eV)

CONCLUSION

We have investigated Xe scattering from the graphite(0001) surface at hyperthermal incidence energies using molecular dynamics simulations.

The conservation of the tangential component of the momentum was directly showed, and especially the normal component of the momentum obeys the Hard-Cube model well. This high adaptation to the Hard-Cube model was realized by the "weak" interplanar potential and the "strong" intraplanar potential of the graphite surface. And the deformation of the graphite surface like a trampoline net and the Xe atom like a trampoliner was also supported from the MD simulations.

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