Trampoline motions in Xe-graphite (0001) surface scattering

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Abstract

We have investigated Xe scattering from the graphite(0001) surface at hyperthermal incident energies using a molecular beam-surface scattering technique and molecular dynamics simulations. For all incident conditions, the incident Xe atom conserves the momentum parallel to the surface and loses approximately 80% of the normal incident energy. The weak interlayer potential of graphite disperses the deformation over the wide range of a graphene sheet. The dynamic corrugation induced by the collision is smooth even at hyperthermal incident energy; the graphene sheet moves like a trampoline net and the Xe atom like a trampoliner.

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1. Introduction

Knowledge of an interaction potential is of key importance in understanding gas-surface dynamics. Particularly energy transfer dynamics between a gaseous particle and surface atoms play important roles in surface reactions induced by collision of energetic particles, known as "collision-induced process" or "hammering" [1-3]. A Molecular beam-surface scattering technique is one of the most powerful tools for probing a gas-surface interaction potential. A variety of molecular beam experiments have been performed, particularly between a rare gas atom and a clean metal surface [4-6]. From Xe-Pt(111) surface scattering experiments Rettner et al. found the existence of two scattering regimes; the structure scattering is dominant at high incident energies and the thermal scattering at low energies [7]. The former is the scattering from a corrugated surface and the latter from a smooth surface. Barker et al. carried out a molecular dynamics (MD) simulation with their empirical potential for the Xe-Pt(111) system and reproduced a wide range of experimental data [8].

Although many scattering experiments have been reported, most of them were performed on the system in which an impinging particle was lighter than a surface atom, such as Ar/Pt and Xe/Pt [1-8]. Less is known about the scattering system in which a gaseous atom is heavier than the surface atom. Since the heavy inert gas atom has a large van der Waals radius, scattering in those systems involves the collision between an impinging atom and an ensemble of the surface atoms. The collision of an atom with the heavy mass and the large radius may lead to the effective dissipation of the kinetic energy through phonons [9,10].

In the present letter we study the non-reactive scattering of a massive Xe atom from a graphite(0001) surface. Previously we investigated the same system at thermal incident energies and discussed the degree of the energy transfer [11]. Någård et al. reported molecular beam experiments and MD simulations of Xe scattered from the graphite surface for a wide range of incident conditions [12]. Although their MD simulations gave good agreement with the experiments at low incident energies, deviations came out at higher energies. It is probably because the distance from a sample to a detector was too short to determine the reliable translational energies of the scattered atoms. In order to derive a more detailed understanding of the Xe-graphite interaction at hyperthermal incident energies, we have carried out the Xe-graphite surface scattering experiments using the apparatus in which the distance between a sample and a detector is long to give the accurate velocity distributions.

2. Experiment and molecular dynamics calculations

Experiments were performed in a molecule-surface scattering apparatus, which has been described in detail previously [13]. Prior to each measurement, a graphite plate (MB grade, Mosaic Spread = 0.4 ± 0.05°) purchased from Matsushita [14] was annealed to remove contamination at 550 K for several hours. This temperature was held during the measurement. The molecular beam was formed by a supersonic expansion of a gas mixture from a Pt nozzle with a diameter of 30 μm. The translational energy of the incident beam was controlled by varying the seeding ratio of Xe to He and/or the stagnation temperature. A time-of-flight (TOF) technique was

employed to determine the velocity distribution of incident and scattered atoms. The molecular beam was pulsed with a rotating mechanical chopper disk placed before entering the sample chamber. In order to elongate a flight length between the sample surface and an ionizer region, ions formed by the electron bombardment were extracted toward the reverse direction with respect to the direction of the incoming neutral beam and introduced to the quadrupole mass filter. The flight length was 34.7 cm, which was long enough to obtain accurate velocity distributions for particles at hyperthermal energies. In the present study the ion lens system was modified to ensure the reflection of the Xe^+ ions originating from the hyperthermal Xe atoms, and thus the detection efficiency of the atoms was dramatically improved.

The molecular dynamics (MD) method was used to simulate the collisions of a Xe atom with a graphite surface [16]. Six sheets of 384 carbon atoms in each graphene sheet were taken into consideration. We have used a model potential of graphite for MD simulation; a Lennard-Jones (6,12) potential was assumed for an interplanar C-C pair (ε = 2.40 meV, σ = 3.37 Å) and the Brenner potential [17] was used for carbon atoms in the same graphene sheet. The potential model is similar to that employed by Någård et al. [12]. While Någård et al. adopted a single translational energy for the incident atoms, a velocity spread of the incident beam has been taken into consideration in our MD calculation.

3. Results

3.1. Xe-graphite(0001) surface scattering experiment

Figure 1 shows a TOF spectrum of the direct beam [Fig. 1(a)] and those of the scattered Xe atoms detected at the scattering angles (θ_f) of 45, 60, 70, and 80° with respect to the surface normal. The incident angle θ_i is 35°, the initial kinetic energy E_i is 1.56 eV, and the surface temperature T_s is 550 K. Intensities of TOF spectra are scaled in such a way that the peak intensity in the TOF spectra of θ_f = 60° is normalized to 1.0. The scattered spectra exhibit only one sharp velocity component almost as sharp as that of the incident beam. Thus, the component is ascribed to the scattered atoms from the direct-inelastic scattering process [8,9]. All the TOF spectra have been well fitted to one shifted Maxwell-Boltzmann distribution.

Figure 2 shows the energy ratio E_f/E_i, i.e., the mean final translational energy E_f of the scattered atoms over the mean incidence energy E_i, as a function of the scattering angle. The incident angles are 15° [Fig. 2(a)], 35° [Fig. 2(b)] and 60° [Fig. 2(c)] and the initial kinetic energies were varied from 0.45 to 3.6 eV at each incident angle. The solid lines in Fig. 2 are the calculated energy ratios assuming that the momentum parallel to the surface is conserved for each incident angle. The strict parallel momentum conservation (PMC) requires that E_f/E_i equals $(\sin\theta_i / \sin\theta_f)^2$ for all final angles [15]. For all incident angles, it is apparent that the energy ratio curves follow the prediction of PMC even at hyperthermal incident energies.

3.2. Comparison with molecular dynamics simulation

We have simulated Xe atom-graphite(0001) surface scattering using the Brenner-LJ potential model. Figure 3(a)-(c) show the angular flux distributions for T_s = 550 K, θ_i = 35°, and E_i = 0.45, 1.56 and 3.29 eV. With the increase of E_i, the spread of the distribution decrease and the peak angle of the distribution slightly shifts and converges to θ_f = 60° in both experiment and simulation results. The narrowing of the flux distributions with increasing energy is qualitatively consistent with the predictions of PMC. The width of the flux distribution depends on the velocity of the surface atoms, and its dependence decreases as E_i increases [15]. At θ_f = 60°, approximately 80% of the normal incident energy of the Xe atom is lost and transferred to the phonon modes of the graphite surface.

The experimental and calculated E_f/E_i ratios are shown in Fig. 3(d)-(f). For all E_i the calculated ratios agree with both the experimental results and the PMC predictions, although a slight deviation is observed at high incident energy. The simulation using the Brenner-LJ potential model has essentially reproduced the experimental results.

4. Discussion

We have carried out Xe-graphite(0001) surface scattering experiments and Molecular Dynamics simulations. In both experimental and MD simulation results of Xe-graphite scattering at hyperthermal incident energies, the direct inelastic scattering process is only observed.

The angle-resolved energy ratios in Fig. 2 show the parallel momentum conservation of the incident Xe atom. This result represents that

the Xe-graphite potential surface is flat ranging from 0.45 eV to 3.62 eV of the incident energies. In Xe/Pt(111) system [7] the potential energy surface is flat at the incident energy of less than 1 eV, while the corrugation of the gas-surface potential is observed at high incident energies. In general, when the incident atoms with high incident energies penetrate deeply into the repulsive part of the gas-surface potential, the corrugation emerges in the potential energy surfaces. In Xe/graphite(0001) system the repulsive wall of the interaction potential between a Xe atom and surface carbon atoms may be moved away upon the collision because of the weak interaction between graphene layers. As a result, the potential energy surface between a Xe atom and a graphite surface is flat even at high incident energies.

Någård et al. reported that the energy ratios E_f/E_i appreciably deviated from the PMC, especially for high incident energies [12]. The discrepancy must be partly due to the fact that the surface-ionizer distance (4.5 cm) in their apparatus is too short to give the accurate speed distributions, whereas in the present study the surface-ionizer distance is sufficiently long (34.7 cm).

As shown in Fig.3, the energy ratios by MD simulations reproduce the experimental data within error bars. In the small θ_f in Fig. 3(d), there are two points that deviate significantly from the experimental results. Because the low intensity of flux at these angles leads to the small number of sampling in the simulation, it is no use to discuss whether it is due to the statistical errors or the fault of the simulation. Since all data except the above points reproduce the experimental results, the MD calculation using the Brenner-LJ potential model essentially simulates the real situation of

the scattering; the details of the scattering process can be deduced from the MD simulation.

When the Xe atom impinges on the graphite surface, the displacements of many carbon atoms take place in the same phase. Figure 4 shows one snapshot of a Xe-graphite surface collision obtained from MD simulation for E_i = 3.5 eV, T_s = 550 K and θ_i = 35°. According to the van der Waals radius of Xe (218 pm) and the C-C bond distance (142 pm) of the graphene, the collision of Xe would involve two to six surface atoms. Since the impact that the surface atom receives is larger as the mass of incident atom is larger, a heavy Xe atom can push down numbers of surface atoms. Furthermore, since the inter-layer interaction is weak but the intralayer interaction is strong, atoms in the same layer move downward in the same phase upon the collision. In fact, the snapshot shows that at least 12 atoms in the first layer move in the same direction simultaneously. In the movie obtained by the MD simulation, the above movements are distinguishable from the thermal vibration of the layer.

The surface deformation leads to the dynamic corrugation in the gas-surface interaction potential [9-10]. Since the weak interlayer potential of graphite disperses the deformation over the wide range of a graphene sheet, Xe cannot penetrate deeply into the repulsive part of the gas-surface potential even if the Xe atom has hyperthermal incident energy; the Xe atom is scattered from the smooth surface of graphite even at hyperthemal incident energy. Schematically, the topmost graphene sheet moves like a trampoline net and the Xe atom acts like a trampoliner.

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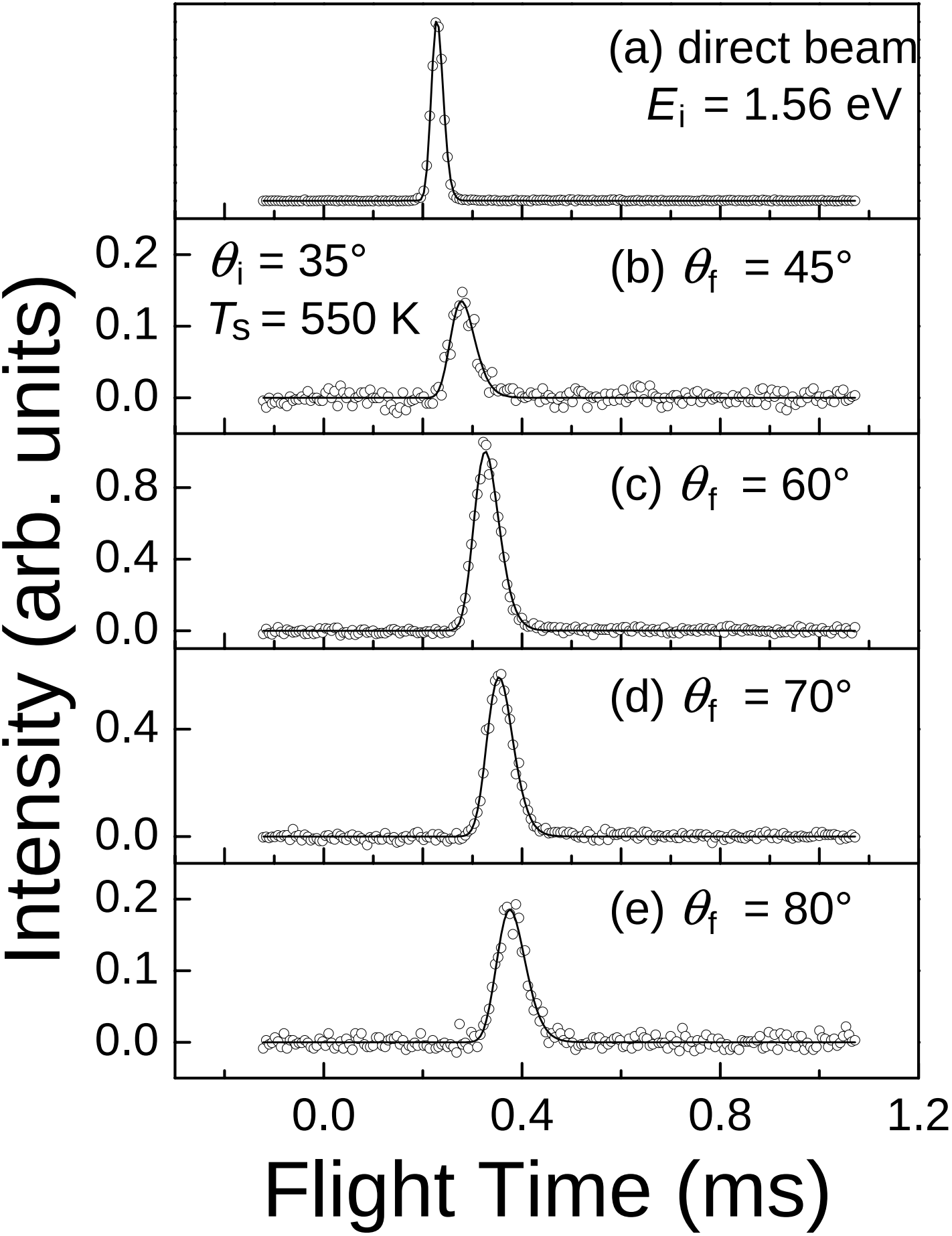
Figure Caption

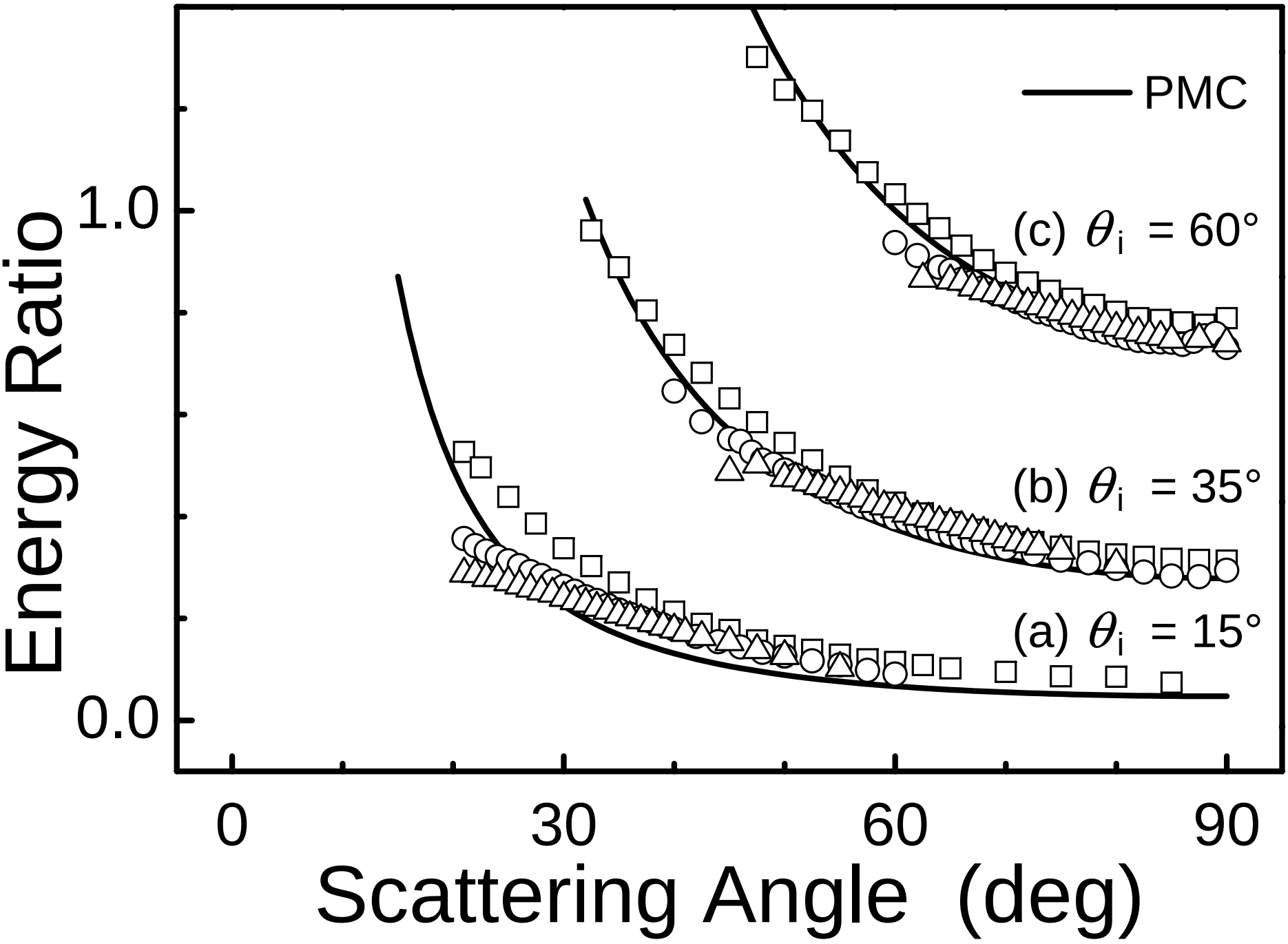
Fig. 1. TOF spectra of (a) the incident Xe beam (E_i = 1.56 eV) and the atoms scattered from the graphite surface for T_s = 550 K, θ_f = (b) 45°, (c) 60°, (d) 70°, and (e) 80°. The lines are the best-fit distributions (flight length = 34.7 cm).

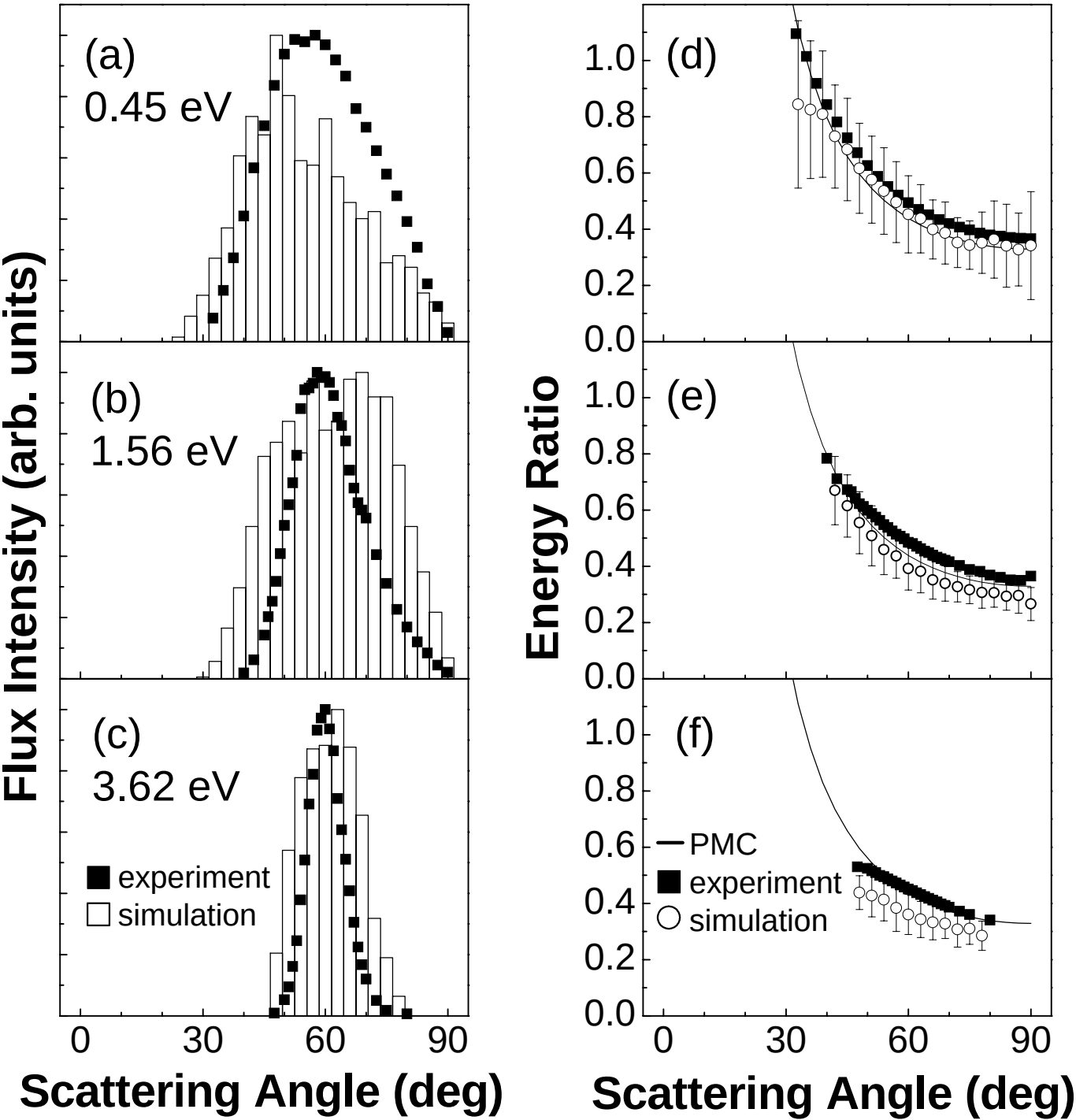
Fig. 2. Variation of the mean final energy relative to the incident energy (E_f /E_i) for Xe atoms scattered from the graphite(0001) at T_s = 550 K for θ_i = (a) 15° , (b) 35° and (c) 60°. The initial kinetic energies in eV are (a) 0.45(□), 1.56(○) and 3.29(△); (b) 0.45(□), 1.65(○) and 3.62(△); (c) 0.45(□), 1.63(○) and 3.49(△). The curves are theoretical E_f /E_i ratios expected for the strict parallel momentum conservation (PMC).

Fig. 3. Comparison of molecular dynamics results with experiment for θ_i = 35°, E_i = 0.45, 1.56, and 3.62 eV, and T_s = 550 K. The angle-resolved flux distributions of scattered Xe atoms and the angle-resolved energy ratios are shown in (a)-(c) and (d)-(f), respectively; ■: experiment, ○: simulation. The lines in (d)-(f) are the PMC prediction.

Fig. 4. A snapshot of the trampoline motions from the MD simulation calculations for θ_i = 35°, E_i = 3.5 eV, and T_s = 550 K.


(a) direct beam
E_i = 1.56 eV
θ_i = 35°
T_S = 550 K
(b) θ_f = 45°
(c) θ_f = 60°
(d) θ_f = 70°
(e) θ_f = 80°
Intensity (arb. units)
Flight Time (ms)
0.0
0.1
0.2
0.4
0.8
1.2


PMC
(c) θ_i = 60°
(b) θ_i = 35°
(a) θ_i = 15°
Energy Ratio
1.0
0.0
0
30
60
90
Scattering Angle (deg)


(a)
0.45 eV
(b)
1.56 eV
(c)
3.62 eV
experiment
simulation
Flux Intensity (arb. units)
0
30
60
90
Scattering Angle (deg)
(d)
(e)
(f)
PMC
experiment
simulation
Energy Ratio
0.0
0.2
0.4
0.6
0.8
1.0
0
30
60
90
Scattering Angle (deg)