Dynamics of collision-induced desorption: Ar–Xe/Pt(111)

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(November 15, 1996)

Abstract

We have performed a detailed study of collision-induced desorption of Xe from Pt(111) by hyperthermal Ar atoms striking the surface. The study combines extensive molecular beam experiments with detailed molecular dynamics calculations in an effort to quantify fully and to understand in detail the dynamics of this model system. The calculations employ accurate semi-empirical potential energy functions for all relevant interatomic interactions. We have characterized the CID process with respect to incidence energy, E_{i}, angle, θ_{i}, and substrate surface temperature, T_{s}, for both the isolated adsorbate and the Xe/Pt(111) monolayer. The generally good agreement of the calculated results such as the desorption yield and desorbate energy and angular distributions with the experimental measurements demonstrates that the calculations capture the most important aspects of the CID processes.

I. INTRODUCTION

Most of our knowledge of the dynamics of gas–surface reactions has been obtained by studying carefully chosen elementary systems. The results of such studies can provide great insight into the mechanisms of important catalytic cycles. If we are to bridge the "pressure gap" between (low pressure) studies and (high-pressure) catalysis, however, we must be sure to consider all relevant processes. In many "real" systems, it seems likely that collision-induced chemistry can play an important role. Any comprehensive model of heterogeneous catalysis must therefore include reactions induced by the bombardment of impinging species. The simplest of these processes is collision-induced desorption (CID), where an incident species transfers sufficient energy to an adsorbate to cause it to leave the surface.

Despite the importance of such phenomena, there have been relatively few relevant experimental or theoretical studies [1–9]. The first experimental observation of CID was reported by Beckerle and coworkers [2,3], who scattered Ar beams from CH_4 adsorbed on Ni(111). More recently, Szulczewski and Levis observed the CID of NH_3 [5,6] and C_2H_4 [7] from Pt(111). Both groups analyzed the results in terms of simple hard cube and sphere models [2–7]. Beckerle and coworkers were able to rationalize the dependence of the CID cross section for low coverages on incidence energy and angle. Szulczewski and Levis argued that it is possible to determine the binding energy from the energy of the desorption threshold. Zeiri and coworkers [1] had pointed out earlier that analysis of the states of the scattered and desorbed species should provide information on the binding properties of adsorbate. Zeiri and coworkers [1,8,9] have carried out detailed dynamical studies of the CID process using a classical molecular dynamics approach. Although instructive, the value of this work is limited by uncertainties associated with using only approximate (Lennard-Jones) interaction potentials.

In this paper, we describe our own recent experimental and theoretical studies of CID dynamics, concerning the CID of Xe from Pt(111) induced by collisions of hyperthermal Ar. We have combined molecular beam experiments with detailed molecular dynamics calculations in an effort to quantify fully the dynamics of this model system. One primary aim of this study has been to understand the dynamics of CID from dense adsorbate overlayers. The calculations employ accurate semi-empirical potential energy functions for all interatomic interactions – Xe–Pt(111), Xe–Xe, Ar–Pt(111), Ar–Xe, and Pt–Pt. We have characterized the CID process with respect to incidence energy, E_i, angle, θ_i, and substrate surface temperature, T_s, for both the isolated adsorbate and the Xe/Pt(111) monolayer. Our characterization goes well beyond previous studies by including an analysis of the desorbate state with respect to energy and angular distributions. The first results of this study, a comparison of measured and calculated desorption yields for monolayer Xe coverage, was given in Ref. [10].

The collision-induced experiments are described briefly in Section II whereas the measured data are discussed and compared with theory in Section IV B. Our model for the interatomic interaction potentials for the Ar/Xe/Pt(111) system is presented in Section III A and its descriptions of some of the characteristic physical properties of this system are discussed in relation to experiments in Section III B. The calculational details of the classical molecular dynamics are given in Section III C. Our results from the molecular dynamics simulations for collision-induced desorption of isolated Xe adsorbates and from the Xe monolayer are presented and discussed in Section IV. Finally, a short summary of our study and some concluding remarks are given in Section V.

II. EXPERIMENTS

The apparatus and methods for studying gas-surface scattering have been described in detail previously. [11–13] A supersonic beam of Ar was directed at the Pt(111) sample held on a manipulator that gave fine control of the incidence angle and surface temperature. The mounting of the Pt(111) crystal was such that scattering plane (containing the surface normal and the beam axis) intercepted the (111) face close to the $\langle 1\bar{2}1 \rangle$ azimuth. The surface was cleaned by Ar-ion sputtering (500 eV) and by flashing to 1300 K. Prior to experiments, contamination levels were below our Auger detection limits (1%). We also obtained sharp LEED patterns and He scattering gave a specular peak with a width indistinguishable from the instrumental resolution of 1.6°. The Xe/Pt(111) layer was prepared by cooling the clean surface to 90 K and exposing it to Xe from an auxiliary beam. We determined Xe coverages by integrating temperature-programed desorption areas. Desorption yields were determined from the fall in coverage caused by a given exposure to the Ar beam.

The Ar translational energy was varied by seeding in He and by varying the tungsten source temperature up to 2300 K. The Ar beam energies were determined from flight times between a high-speed chopper and a differentially-pumped rotatable mass spectrometer. This device was also used to record the time-of-flight and angular distributions of the desorbed Xe atoms. We obtained angular distributions using phase sensitive detection referenced to the chopper and processed with a lock-in amplifier. The TOF distributions were analyzed to yield the velocity distributions of the desorbed atoms as described previously. [11,12] The analysis was the same as that employed in gas-surface reaction studies, [13] where the incident and desorbed species are also different.

III. MODEL

A. Interaction potentials

One of the main motivations for our study of collision-induced desorption of Xe on Pt(111) by Ar atoms has been that there exist good empirical models of the interatomic interaction potentials. These models suggest the following decomposition of the total interaction potential among the Ar atom, the adsorbed Xe atoms, and the substrate Pt atoms with positions denoted by $\mathbf{r}$, $\mathbf{r}_i$, and $\mathbf{r}_n$, respectively:

$$V(\mathbf{r},\{\mathbf{r}_i\},\{\mathbf{r}_n\}) = V_{\text{ia}}(\mathbf{r},\{\mathbf{r}_i\}) + V_{\text{is}}(\mathbf{r},\{\mathbf{r}_n\}) + V_{\text{as}}(\{\mathbf{r}_i\},\{\mathbf{r}_n\}) + V_{\text{aa}}(\{\mathbf{r}_i\}) + V_{\text{ss}}(\{\mathbf{r}_n\}). \quad (3.1)$$

We shall now present and discuss in turn the modeling of the different potential terms in Eq.(3.1).

1. $V_{\rm as}$: Xe–Pt(111)

A unique feature of the Xe–Pt(111) system is that there exists an empirical potential energy function that is consistent with a larger range of dynamical and equlibrium experimental data than for any other gas-atom surface system. This function was developed by Barker and Rettner [14] and is given by

$$V_{\rm as}(\mathbf{r},\{\mathbf{r}_n\}) = \sum_n v_{\rm BM}(|\mathbf{r}-\mathbf{r}_n|) + V_{\rm nl}(z') + \sum_n v_{\rm vdW}(|\mathbf{r}-\mathbf{r}_n - h_{\rm a}\hat{z}|). \tag{3.2}$$

The repulsive branch consists of a pairwise sum of short range Born-Meyer potentials,

$$v_{\rm BM}(r) = A\mathrm{e}^{-\alpha r}, \tag{3.3}$$

and a non-local potential term that describes the softening of the interaction of the Xe atom with the Pt surface ion-cores by the delocalized conduction electrons. This term is given by

$$V_{\rm nl}(z') = \frac{BC\exp(-\beta z'))}{B + C\exp(-\beta z')} \tag{3.4}$$

and depends only on the normal distance, $z' = z - \langle z_s\rangle$, of the Xe atom from the position of the local surface that is defined as

$$\langle z_s\rangle = {\sum_n}' \frac{z_n \exp(-\delta(\mathbf{r}_n - \mathbf{r})^2)}{\sum_n' \exp(-\delta(\mathbf{r}_n - \mathbf{r})^2)}. \tag{3.5}$$

Here the prime denotes that the sum is only taken over atoms in the first layer. The attractive branch in Eq.(3.2) represents the van der Waals interaction and is modelled by a pairwise sum of noncentral potentials that devolves from the central potential

$$v_{\rm vdW}(r) = -\frac{C_6}{r^6}D(r). \tag{3.6}$$

Here the damping function,

$$D(r) = \begin{cases} \mathrm{e}^{-(r_0/r-1)^2}, & r \le r_0, \\ 1, & \text{otherwise} \end{cases}, \tag{3.7}$$

saturates the interaction when the atom comes closer to the surface than r_0. The correct values of all the potential parameters except for r_0 are listed in Ref. [14] and the correct value for r_0 is given in Ref. [15].

2. $V_{\rm aa}$: Xe overlayer

The interactions between Xe atoms have been very well characterized in the gas-phase and an accurate empirical pair potential $v_{\rm HFD-B}$ was proposed by Aziz and Slamann [16]. We employ this potential and represent the interactions between the Xe atoms in the adlayer as

$$V_{\rm aa}(\{\mathbf{r}_i\}) = {\sum_{i,j}}' v_{\rm HFD-B}(|\mathbf{r}_i - \mathbf{r}_j|), \tag{3.8}$$

where the prime denotes that the sum is taken over pairs of different Xe atoms. No attempts have been made to take into account the small nonadditive interactions arising from either many-body dispersion interactions within the layer and with the substrate or between the dipoles induced by the adsorbed Xe atoms.

3. $V_{\rm is}$: Ar–Pt(111)

The details of the interaction between the incident Ar atom and the Pt surface are only important at sub-monolayer coverages. Recently, a simple empirical potential energy function that is consistent with available experimental data such as scattering data for a wide range of scattering conditions was determined by Kulginov and coworkers [17] for this system. This function is given by

$$V_{\rm is}(\mathbf{r}, \{\mathbf{r}_n\}) = \sum_i v_{BM}(|\mathbf{r} - \mathbf{r}_i - h_{\rm r}\hat{z}|) + \sum_i v_{\rm vdW}(|\mathbf{r} - \mathbf{r}_i - h_{\rm a}\hat{z}|). \tag{3.9}$$

where the potentials v_{BM} and $v_{\rm vdW}$ are defined in Eqs.(3.3) and (3.6), respectively and the potential parameters are listed in Ref. [17]. The attractive branch of the potential in Eq. (3.9) has thus the same functional form as the corresponding branch for the interaction potential of Xe with Pt, whereas the repulsive branch is simpler than the one for Xe with Pt. The smoothing of the potential corrugation of the repulsive branch by the conduction electrons is modeled by displacing the force centers in the Born-Meyer potentials.

4. $V_{\rm ia}$: *Ar–Xe overlayer*

For the incidence energies of interest in this work, it is important to have a good description of the repulsive branch of the interaction between the incident Ar atom and the adsorbed Xe atoms. The empirical gas-phase potential energy function that was developed by Aziz and van Dalen [18] fulfils this requirement and gives also an overall good representation of this interaction. Based on this potential, we have represented the interaction of the Ar atom with Xe overlayer by

$$V_{\rm ia}(\mathbf{r}, \{\mathbf{r}_i\}) = \sum_i v_{\rm HFD-B}(|\mathbf{r} - \mathbf{r}_i|). \tag{3.10}$$

For computational convenience we have represented the repulsive part of Ar–Xe interaction with a HFD-B functional form, as used in the representation of the Xe–Xe interaction, instead of the original HFD-C form developed by ziz and van Dalen. The resulting values for the repulsive potential parameters in the HFD-B potential are $A^* = 5.23184 \times 10^4$, $\alpha^* = 5.95714$, and $\beta^* = -5.66398$ in the standard notation, as used, for instance, by Aziz and Slamann [16].

5. $V_{\rm ss}$: *Pt substrate*

We use a simple nearest neighboring central force model for the interactions between the Pt atoms [19]. This model is known to give a good representation of the high frequency part of the bulk phonon spectrum, which is of primary importance in this work The resulting potential is given by,

$$V_{\rm ss}(\{\mathbf{r}_n\}) = \sum_{<n,n'>} \frac{k_1}{2}(|\mathbf{r}_n - \mathbf{r}'_n| - r_{\rm eq})^2 \tag{3.11}$$

where the sums are taken over nearest neighboring atoms with the equlibrium interatomic distances $r_{\rm eq}$. The value of 2.845 eV/Å^2 for $\frac{k_1}{m_{\rm Pt}}$ is chosen to reproduce the maximum bulk phonon frequency $\omega_{\rm max}$ of ~ 22 meV for Pt. We keep the same value for the force constant in the surface region as in bulk because the question about the proper values of the force constants in the surface region is a controversial matter [20]. Note that the total potential in Eq. (3.11) is weakly anharmonic, which is a useful feature for establishing thermal equlibrium in the molecular dynamics.

B. Characteristic physical properties of the Ar-Xe/Pt(111) system

Based on our interaction potential model, we shall now discuss in relation to experiments the calculated properties of the Ar-Xe/Pt(111) system such as binding geometry and energies, vibrational modes and frequencies and some other features of the total interaction potential that are relevant for CID.

The equilibrium position for an isolated Xe atom adsorbed on the Pt(111) surface is at the top site with a distance of 3.3 Å from the underlying Pt atom surface plane. There exists no definitive experimental evidence for this adsorption site. The binding energy of the Xe atom on the static surface is 254 meV with a small potential barrier of only 24 meV between two neighboring equilibrium sites. This binding energy is in rather good agreement with the value of $\sim$ 280 meV for the measured isosteric heat of adsorption in the zero-coverage limit. [21] Among the adsorbate vibrational modes, the perpendicular mode has the highest vibrational energy of 4 meV and is well described by classical mechanics at 90 K. This vibrational energy is well below the value of 22 meV for the maximum phonon energy of the Pt substrate. The binding energy of the Ar atom on the static Pt(111) surface is $\sim$ 80 meV with an equilibrium position of 3.4 Å from the first lattice plane of Pt atoms.

The equilibrium structure of the monolayer of Xe on Pt(111) is a $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice with the Xe atoms in the same adsorption geometry as for the isolated Xe atom. The pairwise interactions between the Xe atoms make the binding energy of a single Xe atom in the monolayer to be 112 meV larger than for the isolated adsorbed Xe atom. In addition, the central interadsorbate forces introduce a small dispersion of the lateral vibrational modes of the Xe atoms while the resulting dispersion of the perpendicular vibrational modes is negligible.

The characteristic features of the interaction of the Ar atom with the Xe monolayer is quite different from the Ar–Pt(111) interaction. The relatively large value of 4.8 Å for the Xe-Xe separation in the monolayer compared to the Ar–Xe dimer equilibrium distance of 4.1 Å makes the Ar interaction with the Xe monolayer to be highly corrugated. In fact, at the hollow site on the monolayer the static interaction potential of Ar with the surface has a saddle point at the equlibrium position of the monolayer. The saddle point energy is $\sim$ 2.7 eV of which Ar–Pt interaction contributes with ~ -0.1 eV. Thus there is a relatively low potential barrier for penetration of the Ar atom through the Xe monolayer.

C. Method of calculation

The calculations were based on molecular dynamics using a slab geometry with periodic boundary conditions in the lateral directions. The Pt surface was represented by a slab with 4 layers and a rectangular surface cell. To accommodate a $(\sqrt{3}\times\sqrt{3})R30^\circ$ overlayer of Xe on the (111) face, the axis of the surface cell were oriented along $[1\bar{1}0]$ and $[11\bar{2}]$ directions of the (111) face and contained 12×16 atoms in each layer. In the case of a single adsorbate a smaller slab with 6×8 atoms in each layer was found to be sufficient.

The effects of energy dissipation into the solid have been modeled by Langevin dynamics [22]. Random and friction forces, as related by the fluctuation–dissipation theorem, [23] were applied in all directions of the atoms in the third layer of the slab while keeping the atoms clamped at their equilibrium positions in the fourth layer. The value for the friction coefficient was chosen to be $0.167\pi\omega_{\mathrm{max}} \sim 2\times 10^{13}\mathrm{s}^{-1}$ in accordance with Adelmann [22].

The sizes of these slabs were large enough to avoid any problems with the cut-off of the interactions potentials at a distance $R_c \sim 9$ Å except for the long-range van der Waals interactions between Ar and Xe with the Pt surface. For distances larger than R_c from a Pt atom, the long-range parts of the van der Waals attractions in V_{as} and V_{is} have been laterally averaged and fixed in space. The deterministic equations of motion for the incident atom, the adsorbed atoms and the two layers of slab atoms were solved using the velocity Verlet algorithm while the stochastic equations of motion were solved by a variant of the Ermak algorithm that is consistent with the velocity Verlet algorithm [24]. A time-step of about 3 fs was found to be sufficient for convergence of the trajectories.

Some care was needed in the preparations of the initial state of the incident atom, the slab, and the overlayer. The initial position of the incident atom was chosen sufficiently far away from the surface so that the slab atoms and the adatoms had time to reach thermal equilibrium before the incident atom collides with the surface. The initial velocities of the atoms in the slab and in the adsorbed overlayer were randomly sampled from a Gaussian distribution with an average kinetic energy of $k_{\mathrm{B}}T$ in each coordinate while keeping the atoms at their equilibrium positions. The approach to thermal equilibrium was monitored by scrutinizing the mean square amplitudes of the adsorbates and the substrate surface atoms. The equilibration time for the adsorbed overlayer was found to be much longer than for the slab. This effect is caused by the weak coupling of the perpendicular motion of an adsorbate atom to its lateral motion and to the motions of all the other atoms. The equilibration time was shortened to ~ 1.5 ps by assuming that the perpendicular motion to be harmonic and by sampling the initial conditions for this motion canonically.

In the case of the ordered overlayer, the lateral position of the incident Ar atom was randomly sampled over a surface unit cell, whereas in the case of a single adsorbate this position was randomly sampled within a circle with a sufficiently large radius to account for all collisions leading to desorption. The velocity of the incident atom was directed along the same $[1\overline{2}1]$ azimuth of the (111) face as done in the experiment.

We have used two different criteria for finishing the integration of the trajectories. The direct desorption criterion amounts to finishing the integration when there were no more adsorbates with positive energy in the normal direction whereas for the full desorption criterion the integration was not finished until all adsorbates either were stuck at the surface with an energy less than $-3kT$ or had left the surface by passing a distance 15Å from the overlayer. The desorption yield for the monolayer was determined from the average number of desorbates and in the case of a single adsorbate the desorption cross-section is given by the desorption yield times the area of the circle in which the impact parameters were sampled. The Ar atom was assumed to penetrate the Xe monolayer as soon it passed the equlibrium position of the monolayer.

We shall primarily consider direct desorption processes. There are two reasons for doing that. First, we find that indirect desorption events, for which adsorbates that are trapped with larger energies than -3 $k_B T$ and desorbs at a later time, are in a small minority. Second, when considering only direct desorption events it is possible to investigate the dynamics behind CID by comparing with results obtained in the situation when the adsorbate-adsorbate interactions are turned off. However, we shall consider the contribution from both direct and indirect desorption processes in the comparison with experiments. In our presentation of the data for the monolayer, we shall use the definition of desorption cross-section, σ_d that was used by Beckerle and coworkers [3]. Note that this definition is based on incoming flux through the surface plane. The desorption yield, N_d, is directly related to σ_d as

$$N_d = \sigma_\mathrm{d}\Theta_0 \tag{3.12}$$

where Θ_0 is the coverage. In the case of the monolayer $\Theta_0 = 0.050\text{Å}^{-2}$ and N_d=1 corresponds to σ_d=20Å^2.

Most of the final energy and angular distributions of the desorbed atoms were obtained by collecting trajectories in bins over the corresponding variables. We estimated the error bars for the calculated quantities by assuming that the results from different trajectories are uncorrelated. In our comparison with the measured data for the average desorbate energies and polar angle distributions, the circular shape of the experimental detector was modeled by collecting trajectories for the desorbates that deflect by less than an angle of 15° from a fixed direction in the incidence plane (parallel to the $[1\bar{2}1]$ azimuth of the Pt(111) face). Because the calculated quantities are based on a limited number of trajectories of about 1000, we have to use a half angle for the detector that is appreciably larger than the half angle of about 2° for the experimental detector.

D. The Hard Spheres and Cube model

For the case of the CID of isolated adsorbates, we find that the results of the full MD calculations can be reproduced quite well using a simple model – hard spheres and cube (HSC) model introduced by Beckerle and coworkers. [3] This model is an extension of the hard-cube model, [25,26] which approximates gas-surface scattering in terms of the interaction of a hard sphere with a hard cube. The HSC model additionally treats the adsorbate as a hard sphere.

The HSC model contains several parameters that have to be determined. They are the mass $m_{\rm i}$ and the hard sphere radius $r_{\rm i}$ of the incident atom, the mass $m_{\rm a}$ and the hard sphere radius $r_{\rm a}$ of the adsorbed atom and the equilibrium height $h_{\rm eq}$ of its center above the hard cube with mass $m_{\rm c}$ and the well depth D for the adsorbate. The values of $m_{\rm i}$ and $m_{\rm a}$ are given by the masses of Ar and Xe, respectively, and the value of D is given by the well depth, ~250 meV, for Xe on Pt(111). Among the distance parameters only the parameter combinations $r_{\rm ia} = r_{\rm i} + r_{\rm a}$ and $h = h_{\rm eq} - r_{\rm i}$ are relevant for the dynamics. The parameter $h_{\rm eq}$ is set by the equilibrium height of the Xe atom above the Pt surface layer whereas the values of $r_{\rm ia}$ and $r_{\rm i}$ are somewhat ambiguous because the distances of the classical turning points for the scattering of the Ar atom from the Xe atom and the Pt substrate vary with energy. We have made the compromise by choosing the values for these distances at an intermediate energy of 2 eV. The resulting values for $r_{\rm ia}$ and h are 2.55 and 1.4 Å, respectively. The variation of $r_{\rm i}$ with lateral position of the Ar atom with respect to the substrate is small and is therefore neglected. Finally, the value of $m_{\rm c}$ is not simply the mass of the Pt atom because the Xe atom interacts with several Pt atoms and its value has been choosen to be $\sim 4m_{\rm a}$ so that the calculated desorption threshold at normal incidence is reproduced.

In the HSC model, the collision-induced desorption is determined by the energy gain by the adsorbate after two collisions either by a direct path in which the incident atom collides with the adsorbed atom which in turn collides with the surface or via a mirror path in which the incident atom first collides with the surface before it collides with the adsorbed atom. In our case $m_{\mathrm{i}} < m_{\mathrm{a}} < m_{\mathrm{c}}$, which implies that each encounter among the spheres and the cube involves only a single collision, and for our choice of parameters the desorption threshold is determined by the direct path, E_{th} is given by

$$E_{\mathrm{th}} = \frac{D}{\mu(\mathrm{i},\mathrm{a})(1-\mu(\mathrm{a},\mathrm{c}))\cos^4(\frac{\theta_{\mathrm{i}}}{2})} \tag{3.13}$$

Here $\mu(1,2)$ is equal to the fraction, $\frac{4m_1m_2}{(m_1+m_2)^2}$, of the incidence energy that is transfered in a collinear impulsive collision of two particles with masses m_1 and m_2. The result in (3.13) is a generalization of the result given by Szulczewski and Levis [6] at normal incidence.

IV. RESULTS AND DISCUSSION

We have used molecular dynamics simulations to study the collision dynamics of Ar striking a Xe/Pt(111) surface for a wide range of incidence conditions, systematically varying the incidence energy and angle, and the surface coverage and temperature. We have also carried out a wide range of experiments on this system. In general, the calculations are in excellent agreement with the experimental results. These studies have revealed a very detailed picture of the collision-induced desorption process for this model system. In presenting our findings we focus on understanding the factors that influence the efficiency of CID, and those that determine the angular and energy distributions of the desorbed Xe. We shall begin by presenting results for the CID of isolated Xe adsorbates, which we shall compare with the predictions of a simple model. Then we shall move on in Section IV B to consider CID from a monolayer.

A. CID of isolated adsorbates

In principle the dynamics of the CID of isolated adsorbates are simple. The incident atom collides with the adsorbate either in a direct collision, sending it towards the surface, or via a mirror collision, in which the incident atom first collides with the substrate. In the former case, the adsorbate transfers some energy to the substrate and rebounds away from the surface whereas in the latter case the adsorbate moves away from the surface and some energy was lost in the initial collision of the incident atom with the substrate. If the adsorbate has sufficient momentum normal to the surface, it will escape the potential well and desorb. Given this picture, we might suspect that the important dynamical features could be accounted for by a simple impulsive model. We shall see that such a model, the Hard Spheres and Cube (HSC) model introduced in Section III D, can indeed provide qualitative insight into the CID process. Moreover, we find that with an appropriate choice of model parameters, it is possible to approach quantitative agreement with the full molecular dynamics simulations. We find that all the discrepancies between the results of the HSC model and the MD calculations are caused by the discrete surface lattice structure and in particular its effect on the energy transfer from the Xe atom to the substrate. We begin by examining the factors that govern the desorption cross section, then examine the energy and angular distributions of the desorbed species.

1. Desorption cross section

The desorption cross section for an isolated atom is a function primarily of the energy, $E_{\rm i}$, and angle, $\theta_{\rm i}$, of the incident Ar. Figure 1(a) shows the calculated $E_{\rm i}$ dependence of the CID cross section, $\sigma_{\rm d}$ for $\theta_{\rm i}$=0, 45, and 60°. It is immediately apparent that there is no simple scaling law for these results, because the dependence on $\theta_{\rm i}$ reverses as $E_{\rm i}$ increases. At low energies, desorption increases with decreasing angle, but for $E_{\rm i} \gtrsim 2.2$ eV, large angles are more favorable. It is also clear that the desorption cross section saturates at high energy.

We find that the general form of the dependence on $E_{\rm i}$ and $\theta_{\rm i}$ can be reproduced quantitatively by the HSC model. [3] The curves in Fig. 1(b) show the results of HSC calculations. It is clear that the HSC calculations are in near-quantitative agreement with the full MD simulations. In light of this agreement, we can turn to the HSC model for dynamical insight into the CID process for this system. As recognized by Beckele and coworkers [3], within the HSC model, the desorption cross section increases with increasing energy primarily because the range of impact parameters that give sufficient energy transfer to effect desorption increases with increasing E_i. This cross section cannot exceed the full geometrical cross section [27] for hard-sphere collisions and so saturates at high E_i. The effect is much the same in the full MD calculations, where saturation is a consequence of the finite range of the interaction between the incident atom and the adsorbate. Energy transfer to the perpendicular motion of the adsorbate decreases with increasing θ_i, but the geometrical cross section for collisons increases. The angular dependence of the CID cross section indicates that the former factor dominates at low energies, close to threshold, while the latter factor prevails for $E_\mathrm{i} \gtrsim 2.2$ eV. Both the increase in the cross section with increasing E_i and the dependence on θ_i at high E_i are also affected by an additional effect identified by Beckerle and coworkers [3]. At high E_i and at off-normal incidence, a new pathway for desorption opens up via mirror collisions, in which the incident atom first collides with the substrate before colliding with the adsorbate, thereby increasing the cross section for large incidence angles at high energy.

The energy threshold, E_th, for CID is a consequence of the energy barrier for the adsorbed atom to leave the surface. It is clear that any quantitative model of the CID process should allow E_th to be related directly to this barrier, which for physisorption is simply the adsorption well depth. At energies close to E_th, the CID cross section is determined by the class of trajectories that most efficiently transfer energy to the coordinate associated with the bond breaking. Again, one might expect the HSC model to accurately predict the threshold energy. The dependence of E_th on θ_i predicted by the HSC model is given by Eq. (3.13): E_th=1.0, 1.4, and 1.8 eV at θ_i=0, 45, and 60°, respectively. This result indicates that E_th should increase monotonically with θ_i. In contrast, we find in the MD simulation a non-monotonic dependence on θ_i: E_th=1.15, 1.1, and 1.4 eV at θ_i=0, 45, and 60°, respectively. We find that this dependence of E_th on θ_i is a consequence of the discrete lattice structure of the substrate and cannot be understood in the HSC model.

At normal incidence, we find that the calculated E_th is determined by side-on collisions where the values for the impact parameters b are ~ 0.7 Å, whereas in the HSC model for light-heavy collisions E_th is determined by head-on collisions where b are close to zero. We find that side-on collisions with $b \sim 0.7$ Å are the most efficient ones for desorption because they maximize the energy transfered to the normal motion of the desorbate. The monotic decrease of the normal momentum transfer from the Ar atom to the Xe atom with increasing b is compensated for small b by the more rapid decrease of the normal momentum transfer from the Xe atom to the substrate for impacts away from the atop site. In the HSC model the normal momentum transfer from the sphere to the cube is independent of the impact site on the cube for fixed incident normal momentum and the maximum energy of the motion of the Xe atom normal to the surface is then attained for on-top collisions of the Ar atom.

The dominance of side-on collisions at normal incidence results in a non-monotonic dependence of $E_{\rm th}$ on $\theta_{\rm i}$. The momentum transfered along the direction of the motion of the Xe atom that gives the maximum energy of the normal motion of the Xe atom after the collision with the substrate increases first with $\theta_{\rm i}$ and decreases for larger $\theta_{\rm i}$. This behaviour is in contrast with the HSC model where the corresponding energy transfer decreases monotonically with increasing $\theta_{\rm i}$, which results in a $E_{\rm th}$ that, as stressed earlier, increases monotonically with increasing $\theta_{\rm i}$. The pronounced effect of the discrete lattice structure on the dependence of $E_{\rm th}$ on $\theta_{\rm i}$ is nicely confirmed by MD simulations where the Xe atom is placed in the metastable hollow site. In this case we find as strong dependence on $\theta_{\rm i}$ as in the HSC model: $E_{\rm th}$ = 0.35, 0.55, and 0.70 eV at $\theta_{\rm i}$ = 0, 45, and 60°, respectively as compared to the corresponding result 0.35, 0.48, and 0.62 eV in the HSC model. Note that $E_{\rm th}$ is smaller at the hollow site than in the atop site because the well depth is about 0.02 eV smaller and the energy transfer from the adsorbate to the substrate is also smaller.

2. Energy and angular distributions of the desorbates

So far we have been concerned only with the CID yield and cross section. In order to provide a more complete characterization of the CID process, we have also calculated the properties of the desorbed Xe atoms.

For the CID of an isolated Xe adsorbate, we find that the mean energy of the desorbed

Xe, $\langle E_\mathrm{d} \rangle$, increases approximately linearly with increasing incidence energy. At a given E_i, the $\langle E_\mathrm{d} \rangle$ values increase with increasing θ_i. Figure 2 displays the dependence of $\langle E_\mathrm{d} \rangle$ on E_i and θ_i calculated by MD and within the HSC model. Again, the agreement between the two models is excellent except for some discrepancies at the lowest energies.

The linear dependence of $\langle E_\mathrm{d} \rangle$ on E_i is simply caused by the linear dependence of the energy transfer on E_i in an impulsive collision. In CID, we have two such collisions; the initial collision of the incident Ar atom with adsorbed Xe atom and the subsequent collision of the Xe atom with the substrate atoms. The average energy transfer in the former collision is rather independent of θ_i whereas the energy exchange that is important for desorption, that is the loss of energy of the perpendicular motion of the Xe atom to the substrate, decreases with increasing incidence angle of the Xe atom. These two effects explain the increase of $\langle E_\mathrm{d} \rangle$ with increasing θ_i. The increase of the offset of $\langle E_\mathrm{d} \rangle$ from zero with increasing θ_i is simply related to the corresponding increase of desorption polar angle, which results in an increase of the energy of the lateral motion of the desorbates.

The discrepancies between the HSC model and the MD simulations for $\langle E_\mathrm{d} \rangle$ close to the desorption threshold are, as in the case of the desorption cross section, caused by the effects of the discrete surface lattice structure on the energy transfer from the Xe atom. The small offset of $\langle E_\mathrm{d} \rangle$ at normal incidence that is present only in the MD results just reflects that E_th is determined by side-on collisions. That the value of $\langle E_\mathrm{d} \rangle$ at $\theta_\mathrm{i} = 45°$ relative to its value $0°$ are larger in the MD simulation than in the HSC model is caused by the lees efficient energy transfer from the Xe atom to the substrate for impact of the Xe away from the top site.

Examining the distribution of energies, $P(E_\mathrm{d})$, for the CID of isolated atoms, we find that this distribution extends from essentially zero to $\sim$50% of E_i. Figure 3 compares the MD result for $P(E_\mathrm{d})$ at E_i=4.4 eV and $\theta_\mathrm{i} = 45°$ with the corresponding result in the HSC model. These two distributions are rather similar but the MD result for $P(E_\mathrm{d})$ displays a pronounced two peak structure. This structure is a signature of two different pathways for CID at the prevailing incidence condition – CID by direct or via mirror collisions – and the discrete surface lattice structure. The contributions from the mirror and the direct collisions to $P(E_\mathrm{d})$ have been separated in Fig. 3. As expected, this separation shows clearly in the both cases that the mirror collisions results in higher E_d than for the direct collision. In the former collision the energy transfer to the substrate occurs via the collision of the light Ar atom with the substrate that results in less energy transfer than in latter collision where the heavy Xe atom collides with the substrate. Note that in both cases, two collisions occur before the Xe leaves the surface, which prevents the maximum E_d from reaching the Baule limit of $\sim$70% of E_i for a single Ar/Xe collision. In the HSC model the two contributions from the direct and the mirror collisions are not able to produce two separate peaks in $P(E_\mathrm{d})$ as in the MD simulations. We find that the low energy peak that is only present in the MD calculations is caused by impacts of the Xe atom close to the bridge site.

We have also looked at the angular distribution of desorbed atoms and at the correlations between desorption direction and average final energy. As expected, we find that the desorbate leaves mainly the surface in subspecular directions, $\theta_\mathrm{d} < \theta_\mathrm{i}$, close to the forward direction, $\phi_\mathrm{d} = 0°$, as illustrated by the results in Figs. 4 and 5, which display azimuthal and polar distributions of both the MD simulations and HSC model. The MD results are more or less reproduced by the HSC model. The larger amount of backscattering, $|\phi_\mathrm{d}| > 90°$, and less intensity in directions close to the surface normal in the MD results as compared to the results of the HSC model are both caused by the corrugation of the Xe/Pt surface potential that enhances the scattering angles for impacts of the Xe atom close to the top site. Figure 6 shows the variation of the mean desorbate energy with desorption polar angle. That the largest $\langle E_\mathrm{d}\rangle$ are found in subspecular directions, $\theta_\mathrm{d} < \theta_\mathrm{i}$, can be understood qualitatively from the HSC model. The increase of E_d with θ_d is primarily an effect of the decrease of energy transfer from the Xe hard sphere to the cube with increasing incidence angle of the sphere. We find that the sharp drop of E_d at $\theta_\mathrm{d} \sim 40°$ in the MD calculation compared to the result of the HSC model is a consequence of the site dependence of the energy transfer from the Xe atom to the substrate. For trajectories that result in desorption in directions close to the surface normal the desorbate has to hit the surface close to the top site where the energy transfer to the substrate is maximal. This substrate effect makes the sharp drop of E_{d} at $\theta_{\mathrm{d}} \sim 40^{\circ}$ relatively independent of θ_{i}.

B. CID from Xe/Pt(111) Monolayer

In having characterized the dynamics of CID for isolated adsorbates, we are now in a position to discuss the considerably more complex case of CID from a Xe/Pt(111) monolayer. The extra complexity arises because Xe atoms that have been struck by an incident Ar can themselves collide with other adsorbed atoms before leaving the surface. For the isolated atom case, the adsorbate will desorb once it acquires sufficient momentum away from the surface to escape the gas-surface well. After being struck by the incident atom, the adsorbate loses momentum only in the collision with the substrate. For "mirror collisions", even this one bounce off the substrate is missing. For the monolayer case, however, atoms that have sufficient momentum after bouncing off the substrate may not leave the surface if they lose further momentum to other adsorbed atoms. On the other hand, as we shall see, some adsorbed atoms may leave the surface without being struck by an Ar atom at all. They may acquire the required momentum in an indirect manner from another Xe that was itself struck by an Ar. In addition, the incident atom may collide with more than one adsorbate. One adsorbate can shadow another, thereby rendering certain trajectories inaccessible. For example, while the incident atom can penetrate the monolayer, "mirror collisions" will be very different than for the isolated atom case. Furthermore, as well as affecting whether or not atoms are desorbed, adsorbate-adsorbate interactions affect the energies and angular distributions of those atoms that leave. Simple models are of little value in trying to understand these extra complexities. In this case, we will compare results where possible to the results of experiments performed under comparable conditions. We begin by looking at the CID yield for the monolayer case.

1. Collision-induced desorption yield

Fig. 7 shows the energy dependence of the calculated desorption yield and cross sections for CID from a Xe monolayer for different incidence angles. We present results for surface temperatures of $T_{\rm s} = 0$ (upper panel) and 90 K (lower panel). Note that our classical calculations ignore the zero-point vibrational motion of the atoms, which could be important for the low-energy adsorbate modes at $T_{\rm s} = 0$ K. These results are in relatively good agreement with the experimental measurements of the CID yield. The experimental results for a surface temperature of 90 K are directly compared with the calculated results in Fig.8. Note that the full desorption criterium has been used for the calculated results in this case and that these results show small differences from the results in Fig. 7(b) based on the direct desorption criterium. Moreover, the results are plotted as a function of the so-called "normal energy", $E_{\rm n} = E_{\rm i} \cos^2 \theta_{\rm i}$, which has been used previously as a scaling parameter for CID. Both the experimental and calculated yields increase from a threshold around 0.5 eV to a yield of unity at $E_{\rm n}$ ~3 eV. The good agreement between the predicted and experimental CID yields gives us confidence that the calculations capture the most important aspects of the CID processes.

Comparing the calculated results in Fig. 7 with those of Fig. 1(a) for the isolated adsorbate case we see that the overall cross section is lower for CID from the monolayer at low energies. At higher energies, $E_{\rm i} > 4$ eV, the cross section is similar for the two cases but the saturation at high energies for $\theta_i = 0°$, seen in the isolated adsorbate case, is no longer apparent for the monolayer case. In addition, for $\theta_i = 60°$ the cross section is clearly larger for CID of the isolated adsorbate. The dependence on incidence angle is therefore very different for CID from the monolayer. It is these changes that are responsible for the shift towards normal energy scaling for the monolayer case.

As we mentioned above, there are two important effects on going from the isolated adsorbate to the monolayer. First, certain trajectories are blocked by the "shadowing" of one adsorbate by another, and secondly, Xe atoms that would otherwise leave the surface can collide with other adsorbates that block their escape path, trapping them on the surface. In addition, there is a third effect that becomes important at high energies. Above about 6 eV, when the cross section for desorption exceeds the Xe unit cell area, multiple desorption becomes possible, where more than one Xe desorbs on average for each incident Ar. We will consider this third effect in detail in the next section. For now, let us concentrate on the first two effects.

We can separate the first two effects by carrying out calculations in which we "turn off" the adsorbate-adsorbate interactions. By that, we mean that we turn off the Xe-Xe pair potential. This change allows the desorbing atoms to pass through other adsorbates. Since the Ar-Xe interaction is unchanged, we retain the shadowing effect with respect to the incident Ar. The results of this model calculation are displayed in Fig. 9. While the effect of this change is to increase the cross section for all incidence angles, the enhancement is strongest for large angles. The $\theta_{\rm i} = 60^\circ$ cross section for $E_{\rm i}$ $\sim$4 eV roughly triples on turning off the adsorbate-adsorbate interactions. The result remains well below that for the isolated adsorbate, however, indicating that both the blocking of the incident atom and the blocking of the departing adsorbate reduce the CID cross section for the monolayer compared to the isolated adsorbate case. Furthermore, both of these effects become more important with increasing incidence angle.

Comparing Fig. 7(a) with Fig. 1(a), both of which refer to calculations for a surface temperature of 0 K, we also notice a pronounced increase in the desorption threshold, $E_{\rm th}$, on going from the single adsorbate to the monolayer case. $E_{\rm th}$ for the monolayer case is about twice as large as for the isolated-adsorbate case. We attribute this difference largely to the adsorbate-adsorbate interactions because when these interactions are turned off, the $E_{\rm th}$ values and the behavior of $\sigma_{\rm d}$ close to $E_{\rm th}$ are found to be very similar for the monolayer and the single adsorbate systems. The adsorbate-adsorbate interactions increase the threshold CID behavior in two ways. In addition to the escape-blocking role of the adsorbates, adsorbate-adsorbate attraction increases the binding energy of a Xe atom by $\sim$ 40% in our model and partition the energy deposited by the Ar atom among several adsorbates.

As can be seen in Fig. 10, $E_{\rm th}$ is very temperature dependent. At 90 K, $E_{\rm th}$ is even below its value in the single adsorbate case. As CID for $E_{\rm i}$ close to $E_{\rm th}$ involves rare events, thermal fluctuations that broadens the range of energy transfers associated with the interactions among the incident atom, the adsorbate and the substrate lattice is expected to have significant influence on $E_{\rm th}$. When the adsorbate-adsorbate interactions are turned off, the $T_{\rm s}$ dependence is weak except for $E_{\rm i}$ very close to $E_{\rm th}$. This behavior is evident from a comparison of the solid and open squares for $\theta_{\rm i} = 45°$ in Fig. 9. It is apparent that raising $T_{\rm s}$ has little effect on $\sigma_{\rm d}$ for $E_{\rm i}$ above $\sim$ 1.5eV. Yet this change in $T_{\rm s}$ does have a significant effect on the $E_{\rm th}$.

2. Collision-induced desorption of multiple adsorbates

As seen in both the experimental (Fig. 8) and calculated results (Fig. 7), at sufficiently high energy, each incident atom can induce the desorption of more than one Xe, causing the yield to exceed unity. We can break down the overall CID probability into separate probabilities, P_n, for CID of n Xe atoms by each incident Ar. In Fig. 11, we show the dependence of these probabilities on $E_{\rm i}$ at normal incidence. It is apparent that the Ar atom is able to induce desorption of as many as 6 Xe atoms at $E_{\rm i} = 6$ eV and $T_{\rm s} = 0$K. As already anticipated in the introductory discussion of Section IV B, there are two mechanisms for multiple desorption. Multiple adsorbates can acquire sufficient energy to desorb either by being hit directly by an incident Ar atom or by being hit by another Xe atom. Adsorbate-adsorbate collisions promote desorption of several atoms by distributing $\Delta E_{\rm i}$ over more adsorbates than those being directly involved in the collision with the incident Ar atom. This effect is clearly demonstrated in Fig. 11(c) which displays the energy dependence of P_n when the adsorbate-adsorbate interactions are turned off. This change causes the maximum number of desorbed atoms to fall from 5 to 2 at $E_{\rm i} = 4.4$eV. An increase of $T_{\rm s}$ tends also to decrease the multiple desorption probabilities as can be seen in Fig. 11(b). A peculiar feature at $E_{\rm i} = 6$ eV and 0K is the change of character of the multiple desorption probabilities at $E_{\rm i} = 6$ eV: P_n does not decay rapidly with n. Rather, it is about the same for $n = 2 - 5$. This behavior of P_n is not present at $T_{\rm s} = 90$K.

C. Adsorbate energy and angular distributions

More detailed information about the dynamics of collision-induced desorption can be obtained by analyzing the calculated desorbate energy and angular distributions and the correlations between desorbate energy and angle.

1. Average desorbate energy

For an isolated adsorbate, we found that the mean energy of the desorbed species is essentially proportional to the energy of the incident atom above some threshold energy, as illustrated by Figure 2. The harder the collision, the higher the energy of the atoms after impact. For CID from the monolayer, the situation is far more complex. The energy of the incident atom can be partitioned amongst many adsorbates and any that retain sufficient energy to leave the surface will desorb. This effect leads to a steady increase in the yield, Fig. 7, while "pinning" the mean desorbate energy. Figure 12(a) displays the calculated mean energy for CID at 0 K. Here we see that for $E_{\rm i}$ of 6 eV the mean energy is less than 0.2 eV, about a factor of ten lower than for isolated adsorbates. As before, we have gained insight into this process by turning off the adsorbate-adsorbate interactions. This change results in a large increase in the mean energies, as shown in Fig. 12(b). We believe that the large decrease of $\langle E_{\rm d} \rangle$ on going from the isolated adsorbate to the monolayer is caused by the effective energy transfer among the adsorbates rather than the increase of the well-depth with ~ 0.1eV by the attractive branch of the adsorbate-adsorbate interactions. The remaining differences between the isolated adsorbate case and the monolayer case are largely due to shadowing effects. As discussed already in Section IV C 1, the obstruction of the collinear collisions of the incident atom with an adsorbate by surrounding adsorbates is effective at large θ_i and results in collisions with less energy transfer. The change of character of the collision-induced desorption at $\theta_\mathrm{i} = 0°$ and E_i=6eV, as noted in the behavior of both σ_d in Section IV B 1 and the multiple-desorbate distributions in Section IV B 2, is also revealed here by the dramatic decrease of $\langle E_\mathrm{d} \rangle$ at this incidence condition.

Our calculated CID energies are found to be in good agreement with experimental measurements. Figure 13 displays a comparison of calculated and measured mean desorbate energies. These results refer to Xe atoms desorbed in the direction of the surface normal for $\theta_\mathrm{i} = 35°$. The calculated energies correspond to an average over a 15° range of angles. Note also that the experimental measurements are relevant to the Xe/Pt(111) compressed phase, which has a slightly higher coverage. The main point of this comparison is to show that the desorbate energies are indeed only a small fraction of E_i and rise only slowly as E_i increases.

2. Desorbate energy distributions

We find that not only is the mean desorbate energy low for CID from the monolayer, but the probability of any Xe atoms leaving the surface at high energy is relatively low. Trajectories leading to high energies for isolated adsorbates are blocked either by shadowing of the incident atom or by blocking of the escaping atom. To explore further this point, we show some examples of desorbate energy distributions, $P(E_\mathrm{d})$, in Fig. 14. We compare four calculations, relevant to the monolayer at 0 K, and at 90 K, in Figs. 14(a) and (b); to the monolayer in the absence of adsorbate-adsorbate interactions, Fig. 14(c); and to the isolated adsorbate, Figs. 3.

For CID from the monolayer, the distribution $P(E_\mathrm{d})$ is more or less consistent with a Maxwell-Boltzmann (or thermal) distribution. Noting that such a distribution maximizes the entropy under the constraint that $\langle E_\mathrm{d} \rangle$ is constant, we conclude that there is little dynamical information content in the results. The corresponding energy distribution, $P_\mathrm{MB}(E_\mathrm{d})$, is given by,

$$P_{\rm MB}(E_{\rm d}) = \frac{E_{\rm d}}{(k_B T_{\rm d})^2} \exp(-\frac{E_{\rm d}}{k_B T_{\rm d}}), \tag{4.1}$$

where the effective desorbate temperature, $T_{\rm d}$, is defined as

$$T_{\rm d} = \frac{\langle E_{\rm d} \rangle}{2k_B}. \tag{4.2}$$

The overall good agreement of the calculated $P(E_{\rm d})$ with $P_{\rm MB}(E_{\rm d})$ at the surface temperature $T_{\rm s} = 90$K, when using the calculated value for $\langle E_{\rm d} \rangle$, is illustrated in Fig. 14(b). At $T_{\rm s} = 0$K, the distribution in Fig. 14(a) is peaked at a slightly higher $E_{\rm d}$ than for the statistical distribution. A comparison of the result for $P(E_{\rm d})$ in Fig. 3 with the one obtained for non-interacting adsorbates in Fig. 14(c) shows that the adsorbate-adsorbate interactions plays an important role in generating a statistical-like distributions. This fact is stressed by the comparison of the results for $P(E_{\rm d})$ in Figs 14(c) with $P_{\rm MB}(E_{\rm d})$ when using the calculated value for $\langle E_{\rm d} \rangle$.

The obstruction of mirror-collisions for the monolayer is clearly demonstrated from a comparison between the results for $P(E_{\rm d})$ in Figs 14(c) and 3. The high-energy peak in $P(E_{\rm d})$ for the isolated adsorbate that is not present in $P(E_{\rm d})$ for the monolayer of non-interacting adsorbates. Otherwise the latter distribution is rather similar to $P(E_{\rm d})$ for the isolated adsorbate.

3. Desorbate angular distributions

In the case of CID of an isolated adsorbate, we saw that the desorbed atoms leave the surface primarily towards the specular direction, as shown in Figs. 4 and 5. As we might expect, for CID from the monolayer, the trajectories leading to quasi-specular desorption are blocked, both for the incident atom and for the desorbing atom. The angular distributions for CID from the monolayer are therefore very different from the isolated atom case. Figs. 15 and 16 display the azimuthal and polar angle distributions, $P(\phi_{\rm d})$ and $P(\theta_{\rm d})$, respectively, for the same incidence conditions of the Ar atom as used in the discussion of the results for $P(E_{\rm d})$ in Section IV C 2. Results are presented for the isolated atom, the monolayer without adsorbate-adsorbate interactions, and for the full simulation at a surface temperature of 0 K and 90 K.

By comparing the results for the non-interacting adsorbates in the monolayer with those for the isolated adsorbate, Figs. 15(c) and 4, we can gain insight into the shadowing effects that block and deflect the incident Ar. We see that the $P(\phi_{\rm d})$ distribution exhibits a peculiar double-peak structure. This structure is caused by two different effects. First, the shadowing of the incident Ar by the Xe adsorbates is most effective for trajectories in the incidence plane that passes through the centers of two adsorbed atoms. As the desorption in the forward direction is dominated by collisions in this plane, $P(\phi_{\rm d})$ has a local minimum at $\theta_d = 0°$. Second, incident Ar atoms that are deflected by the first collision often make a second collision with another adsorbate. These secondary collisions result predominantly in desorption of in a direction well out of the incidence plane, which gives rise to the double-peak structure.

In the monolayer case, the calculated $P(\phi_d)$ in Figs 15(a) and (b) are more or less uniform for the two surface temperatures. This behavior is consistent with the statistical (thermal) distribution $P_{\rm MB}(\phi_d) = \frac{1}{2\pi}$. The accompanied loss of memory of the incidence azimuthal angle ϕ_i in $P(\phi_d)$ is mostly an effect of the adsorbate-adsorbate interactions, as demonstrated by a comparison of the result for $P(\phi_d)$ in Figs 15(a) and (b) with the result in Fig. 15(c).

Although the azimuthal distributions are largely statistical, we find the polar angular distributions, $P(\theta_d)$, for the monolayer case are clearly non-statistical. Since the polar angular distribution is integrated over azimuthal angle, $P_{\rm MB}(\theta_{\rm d})$, has the form,

$$P_{\rm MB}(\theta_{\rm d}) = \sin\theta_{\rm d}\cos\theta_{\rm d} \tag{4.3}$$

As illustrated by our calculated results for $P(\theta_d)$ in Figs 16(a) and (b), we find in general $P(\theta_d)$ to be more peaked towards the surface normal, $\theta_d = 0°$, than $P_{\rm MB}(\theta_d)$, in particular, at $T_{\rm s} = 0{\rm K}$.

The peaking of $P(\theta_d)$ towards the surface normal for the monolayer has a simple origin.

Most of the collisions of the Ar atom with the adsorbed Xe atoms leads to trajectories for the Xe atom with a relatively large angle of impact with the substrate. In the situation of non-interacting adsorbates or for an isolated adsorbate, the adsorbate then desorbs at a large off-normal polar angles as shown in Figs 5 and 16(c). In the presence of adsorbate-adsorbate interactions, the Xe atom has to make a collision with neighboring Xe atoms before leaving the surface and that changes the motion of the desorbing atom in a direction towards the surface normal. In the case of the isolated adsorbate or for non-interacting adsorbates, we find that even at normal incidence of the Ar atom $P(\theta_d)$ peaks around $\theta_\mathrm{d} \sim 70°$. Thus the CID of Xe atoms in directions close to the surface normal is a characteristic feature of the adsorbate-adsorbate interactions. The surrounding adsorbates block desorption at large angles from the normal.

These calculations and conclusions are consistent with measurements of the polar angular distribution as a function of coverage. In Fig. 17 we display polar angular distributions measured for CID of Xe by incident Ar with E_i = 1.1 eV and θ_i = 60° at 90 K. It is immediately apparent that the peak of the angular distribution shifts from the normal to the specular as the coverage falls (i.e. as we go from the monolayer towards the isolated adsorbate). The calculated polar angular distributions for the monolayer and the isolated adsorbate in Figs 16(b) and 5, respectively, exhibit the same behaviour. These distributions are integrated over all azimuthal angles and a more direct comparison with the measured distributions are provided by the distributions in Fig. 18, which have been calculated by collecting trajectories for the desorbates that enters a detector aperture in the incidence plane. These distributions are indeed very similar to the measured data in the high and low coverage limits. Because of the small desorption yields close to the desorption threshold and the associated poor statistics in the calculations we have not been able to go down to $E_\mathrm{i} = 1.1$ eV and the calculated data refer to $E_\mathrm{i} = 4.4$ eV.

4. Desorbate energy versus desorbate angle

In addition to the information provided by the angular and energy distributions, we find pronounced dynamical signatures in the correlations between the desorbate energy and the polar angle at which the desorbates leave the surface. This behavior is illustrated by the calculated results for $\langle E_{\rm d}\rangle(\theta_d)$ in Fig. 19. The important trends evident in the results at $T_{\rm s}$=90 K, Fig. 19(b), are in remarkably good agreement with the experimental measurements shown in Fig. 20.

In order to understand this behavior, we begin by considering once again the monolayer of non-interacting adsorbates. In this case the obstruction of trajectories at large $\theta_{\rm i}$ that leads to near-collinear collisions decreases the energy transfer from the Ar atom to the Xe atom and $\langle E_{\rm d}\rangle$ decreases dramatically. The rapid rise of $\langle E_{\rm d}\rangle(\theta_d)$ with $\theta_{\rm d}$ mirrors the rapid increase of $P(\theta_{\rm d})$ at those angles, as shown in Figs 5 and 16(c). In the presence of adsorbate-adsorbate interactions, desorbates that attempt to leave the surface at large θ_d collide with other adsorbates, resulting in large energy and momentum transfers. As already stressed in Sections IV C 1 and IV C 3, this energy transfer results in a dramatic decrease of $\langle E_{\rm d}\rangle$ and desorption in $\theta_{\rm d}$ closer to the surface normal and these effects are also shown by the results for $\langle E_{\rm d}\rangle(\theta_d)$ in Fig. 19(a). As shown in Fig. 19(b), the adsorbate-adsorbate interactions enhance dramatically $\langle E_{\rm d}\rangle$ for large $\theta_{\rm i}$ at $T_{\rm s}$ = 90K. This result is consistent with the $T_{\rm s}$ enhancement of $N_{\rm d}$ as show in Fig. 7.

In contrast to the polar-angle effects, we find no interesting features in the desorbate energy as a function of azimuthal angle that cannot be understood from our results for $P(\phi_{\rm d})$: $\langle E_{\rm d}\rangle$ peaks in the forward direction for the single adsorbate case whereas $\langle E_{\rm d}\rangle$ is relatively independent of ϕ_d in the monolayer case.

5. Penetration of the adsorbate layer

So far we have concentrated on the fate of the adsorbates. In order to complete the characterization of the CID process, we have also examined the fate of the incident Ar. In most cases, the Ar simply scatters from the adlayer. At high energies, however, the incident atom may penetrate the Xe layer, reaching the Pt(111) surface. We find that penetration is most effective for angles close to normal. This behavior is shown in Fig. 21 for surface temperatures of 0 K and 90 K. It is clear that at 0 K, penetration only occurs at very close to normal incidence. The lighter Ar always scatters off of the heavier Xe at an angle close to the specular about the "local normal", which passes through the center of the Xe atom and the point of impact. Only when this direction lies close to the surface plane will the Ar scatter forward, penetrating the Xe layer. Such impacts can only occur for near-normal incidence, as the required impact points are shadowed at large impact angles. One interesting observation is that for normal incidence and 0K, the Ar atom is able to penetrate the adlayer for $E_{\rm i}$ below the static potential barrier of $\sim$ 2.7 eV. This phenomena shows that the Ar atom is able to lower the barrier by pushing the Xe atoms sideways. Thermal fluctuations of the Xe atoms are also able to lower the barrier as can be seen from the dramatic increase of the penetration probabilities at 90K, because the soft lateral adsorbaate vibrational modes have large amplitudes at 90K.

After the completion of this work, we became aware of a new structural study of the Xe/Pt(111) system, [28] which places the adsorbed Xe atoms in the *hollow* sites for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer. This result is surprising, since careful modelling of He diffraction data [29] indicated that the Xe occupies an on-top site. The potential used in the present study has the Xe adsorption minimum at the on-top site for all coverages. This "on-top" potential was developed by Barker and Rettner, [14] only after they had found that potentials with the Xe in the hollow site were inconsistent with the available experimental results. We therefore believe that further studies are required to confirm this new assignment before we should adjust our empirical interaction potential.

A related study for the Xe/Pd(111) system [30] also placed the Xe in the hollow site for the $(\sqrt{3}\times\sqrt{3})R30^{\circ}$ layer, but concluded that Xe atoms occupy on-top sites at low coverages. Assuming that the same result would be obtained for Xe/Pt(111), these new studies do not, therefore, affect our isolated-adsorbate calculations. Since the CID process is so complex for the monolayer case, with strong adsorbate-adsorbate interactions as well as multiple Ar/Xe collisions, we do not believe that results should be sensitive to the position of the Xe relative to the underlying lattice. We nevertheless plan to carry out calculations using a "hollow" potential to check this point.

V. SUMMARY AND CONCLUSIONS

We have examined the dynamics of collision-induced desorption (CID) for a model system, the sputtering of Xe from Pt(111) by incident Ar. From a combination of molecular dynamics (MD) calculations using accurate interaction potentials, and experiments, we have characterized the CID process with respect to incidence energy, $E_{\rm i}$, angle, $\theta_{\rm i}$, and substrate surface temperature, $T_{\rm s}$, for both the isolated adsorbate and the Xe/Pt(111) monolayer. The generally good agreement of the calculated results such as the desorption yield and desorbate energy and angular distributions with the experimental measurements gives us confidence that the calculations capture the most important aspects of the CID processes.

For the case of the isolated adsorbate, CID occurs after two binary collisions, either Ar/Xe followed by Xe/Pt, or Ar/Pt followed by Ar/Xe. In general, the outcome of these collisions can be reproduced accurately using the hard spheres and cube (HSC) model. We find that the predictions of this simple model are in near-quantatitive agreement with those of the full MD calculations, as seen in Figs. 1 and 2. The largest discrepancies occur close to the desorption threshold, where the structure of the underlying Pt lattice, which is not present in the HSC model, becomes important. We believe that the good description of the CID dynamics in this case by the HSC model can be understood from the characteristic physical properties of this system: the low vibrational energies of the adsorbed Xe atoms and the hard repulsive interatomic interactions, which both makes the collisions impulsive, and the small surface corrugation for the physisorbed Xe atom.

In contrast, the dynamics of CID from the monolayer are highly complex, involving many different interactions and collisions. Compared to the case of isolated adsorbates, we find that many trajectories are blocked by other adsorbates that either "shadow" the adsorbate from the incident atom or block the path of the escaping adsorbate. We have sought to separate these two effects by carrying out model calculations with the adsorbate-adsorbate interactions turned off, so that escaping adsorbates were no longer blocked. We find that both effects are important, having the largest influence at large θ_{i} where shadowing and adsorbate-adsorbate collisions drastically change the CID dynamics.

At high E_{i}, above about 5 eV, the cross section for the isolated adsorbate case is close to saturation, Figure 1, due to the limited range of the Ar/Xe interaction potential. In this case, mirror collisions serve to increase the cross section with increasing θ_{i}. For the monolayer case, no such saturation occurs. Rather, the desorption yield exceeds unity as the cross section rises above the size of the Xe/Pt(111) unit cell. For instance, at $E_{\mathrm{i}} = 6$eV and $\theta_{\mathrm{i}} = 0°$ up to six Xe atoms can be desorbed per incident Ar, Fig. 11. Both Xe-Xe collisions and multiple Ar-Xe collisions contribute to the overall yield.

We find that the desorption yield and desorbate properties are quite strongly affected by the surface temperature, even though kT_{s} is much less than the Xe binding energy. The strongest effects of T_s occur close to the threshold energy, which actually falls by about a factor of two on going from 0 K to 90 K, Fig. 10. We believe that the strong T_{s} effects on CID, in particular for the rare desorption events close to the threshold, are an effect of large thermal fluctuations of the Xe atoms that are caused by their relatively small vibrational energies compared to kT_{s}.

ACKNOWLEDGMENTS

The work by MP has been supported by the Swedish Natural Science Research Council (NFR). DK acknowledges support from the Chalmers fund for research collaboration with Eastern Europe and the Swedish Royal Academy of Sciences (KVA). CTR thanks Daniel Auerbach and John Barker for many useful discussions and Donald S. Bethune for assistance with the measurements.

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FIGURES

FIG. 1. Calculated cross section, σ_{d}, for collision-induced desorption of an isolated Xe atom as a function of the incidence energy, E_{i}, and angle, θ_{i}, of the Ar atom. (a) The full molecular dynamics simulation and (b) the results of the hard spheres and cube model. The surface temperature is 0K.

FIG. 2. Calculated mean Xe desorbate energy, $\langle E_{\mathrm{d}}\rangle$, versus incidence energy, E_{i}, and angle, θ_{i}, for an isolated Xe adsorbate. (a) The full molecular dynamics simulation and (b) the results of the hard spheres and cube model. The surface temperature is 0K.

FIG. 3. Calculated Xe desorbate energy distributions, $P(E_{\mathrm{d}})$, for an isolated adsorbate at $E_{\mathrm{i}} = 4.4$ eV and $\theta_{\mathrm{i}} = 45°$. (a) The full molecular dynamics simulation and (b) the results of the hard spheres and cube model. The dashed and dotted lines show the contributions from the direct and the mirror paths, respectively, whereas the solid line shows the total distribution. The surface temperature is 0K.

FIG. 4. Calculated Xe desorbate azimuthal angular distribution $P(\phi_{\mathrm{d}})$, for an isolated adsorbate. The solid line shows the result of the full molecular dynamics simulation whereas the dashed line shows the result of the hard spheres and cube model. The angle ϕ_{d} is measured with respect to the incidence plane. The incidence conditions and surface temperature are the same as in Fig. 3.

FIG. 5. Calculated Xe desorbate polar angular distributions, $P(\theta_{\mathrm{d}})$, for an isolated adsorbate. The solid line shows the result of the full molecular dynamics simulation whereas the dashed line shows the result of the hard spheres and cube model. Note that the distribution is integrated over azimuthal angle. The incidence conditions and surface temperature are the same as in Fig. 3.

FIG. 6. Calculated Xe desorbate energy, $\langle E_{\mathrm{d}}\rangle$, as a function of polar angle, θ_d, for an isolated adsorbate. The solid line shows the result of the full molecular dynamics simulation whereas the dashed line shows the result of the hard spheres and cube model. The incidence conditions and surface temperature are the same as in Fig. 3. The half-angle of the detector aperture is 30°.

FIG. 7. Calculated collision-induced yield, $N_{\rm d}$, and cross section, $\sigma_{\rm d}$, for desorption of Xe from the adsorbed monolayer as a function of the incidence energy, $E_{\rm i}$, and angle, $\theta_{\rm i}$, of the Ar atom at two different surface temperatures $T_{\rm s}$: (a) $T_{\rm s}$=0 and (b) 90K.

FIG. 8. Comparison between measured and calculated desorption yield, $N_{\rm d}$, for the Xe monolayer as a function of incidence energy, $E_{\rm i}\cos^2\theta_{\rm i}$, normal to the surface and for various incidence angles, $\theta_{\rm i}$ of the Ar atom. The experimental and calculated data are depicted by solid and open symbols, respectively. The calculated $N_{\rm d}$ are based on the full desorption criterium.

FIG. 9. Calculated collision-induced yield, $N_{\rm d}$, and cross section, $\sigma_{\rm d}$, for desorption of Xe from the adsorbed monolayer as a function of the incidence energy, $E_{\rm i}$, and angle, $\theta_{\rm i}$, of the Ar atom in the situation when the adsorbate-adsorbate interaction are turned off. The data set that is indicated by solid squares is calculated at a surface temperature of 90K whereas the remaining data sets are calculated at zero surface temperature.

FIG. 10. Calculated threshold behaviour of the desorption yield, $N_{\rm d}$, of Xe from the adsorbed monolayer. The data are shown as a function of incidence energy, $E_{\rm i}$, for various incidence angles, $\theta_{\rm i}$, and at two different surface temperatures: (a) $T_{\rm s}$ = 0 and (b) 90K.

FIG. 11. Calculated multiple desorption probabilities, P_n, of Xe atoms from the adsorbed monolayer as a function of incidence energy, $E_{\rm i}$, at normal incidence: (a) $T_{\rm s}$ = 0K, (b) 90K, and (c) $T_{\rm s}$ = 0K and with adsorbate-adsorbate interactions turned off.

FIG. 12. Calculated average Xe desorbate energy, $\langle E_{\rm d}\rangle$, versus incidence energy, $E_{\rm i}$, for different incidence angles, $\theta_{\rm i}$ in three different situations: (a) Xe monolayer and (b) Xe monolayer where the adsorbate-adsorbate interactions are turned off. All data are calculated for zero surface temperature

FIG. 13. Comparison between measured and calculated mean desorption energies, $\langle E_{\rm d}(\theta_{\rm i})\rangle$, close to the surface normal, $\theta_{\rm i} = 0°$ as a function of incidence energy, $E_{\rm i}$, at the incidence angle $\theta_{\rm i} = 35°$. The measured data refer to a slightly compressed phase of the adlayer whereas the calculated results refer to the monolayer. In the calculation the half-angle of the detector aperture is 15°. the calculated data are based on the full desorption criterion.

FIG. 14. Calculated Xe desorbate energy distributions, $P(E_{\rm d})$, under four different conditions: monolayer at (a) $T_{\rm s} = 0$K and (b) 90K, and (c) monolayer without adsorbate-adsorbate interactions. The incidence conditions are the same as in Fig. 3. The Maxwell-Boltzmann distributions, $P_{\rm MB}(E_{\rm d})$, where the temperatures are calculated from $\langle E_{\rm d}\rangle$ are indicated by dashed lines. Note that the $E_{\rm d}$ scale is different in (c) from (a) and (b).

FIG. 15. Calculated Xe desorbate azimuthal angular distributions, $P(\phi_{\rm d})$, under three different conditions: monolayer at (a) $T_{\rm s} = 0$K and (b) 90K, and (c) monolayer without adsorbate-adsorbate interactions. $\phi_{\rm d}$ is measured with respect to the scattering plane. The incidence conditions for the Ar atom is the same as in Fig. 3.

FIG. 16. Calculated Xe desorbate polar angular distributions, $P(\theta_{\rm d})$, in three different sitautions: monolayer at (a) $T_{\rm s} = 0$K and (b) 90K, and (c) monolayer without adsorbate-adsorbate interactions. The Maxwell-Boltzmann distributions, $P_{\rm MB}(\theta_{\rm d})$, are indicated by dashed lines. Note that the distributions are integrated over the azimuthal angle. The incidence conditions for the Ar atom as in Fig. 3.

FIG. 17. Measured Xe desorbate polar angular distributions, $P(\theta_{\rm d})$, for different coverages Θ.

FIG. 18. Calculated Xe desorbate angular distributions, $P(\theta_{\rm d})$, for (a) an isolated adsorbate and a monolayer at $E_{\rm i} = 4.4$ eV and $\theta_{\rm i} = 60°$. Note that in this case the distributions were calculated by collecting trajectories in an detector aperture with half-angle 15° in the incidence plane and were not integrated over the azimuthal angle as in Figs 5 and 16.

FIG. 19. Calculated mean Xe desorbate energy, $\langle E_{\rm d}\rangle(\theta_d)$, as a function of polar angle θ_d in three different situations: monolayer at (a) $T_{\rm s}$ = 0K and (b) 90K and (c) monolayer without adsorbate-adsorbate interactions. The incidence energy, $E_{\rm i}$, for the Ar atom is 6.0 eV and the incidence angles, $\theta_{\rm i}$, are indicated. Note that the energy scale is different in (c) from (a) and (b).The half-angle of the detector aperture is 30°.

FIG. 20. Measured mean desorption energies, $\langle E_{\rm d}\rangle(\theta_{\rm d})$, as a function of the desorption polar angle, $\theta_{\rm d}$, in the scattering plane and for various incidence angles, $\theta_{\rm i}$, of the Ar atom. Incidence energy of the Ar atom is indicated.

FIG. 21. Calculated probabilities, $P_{\rm p}$, for penetration of the Ar atom through the Xe monolayer as a function of the normal incidence energy, $E_{\rm i}\cos^2\theta_{\rm i}$, for various incidence angles, $\theta_{\rm i}$, and surface temperatures $T_{\rm s}$; (a) $T_{\rm s}$ = 0K and (b) $T_{\rm s}$ = 90K.