

# Molecular dynamics simulations of collision-induced desorption. I. Low coverage N<sub>2</sub> on Ru(001)

Leonid Romm and Micha Asscher

*Department of Physical Chemistry and Farkas Center for Light Induced Processes, The Hebrew University, Jerusalem, 991904, Israel*

Yehuda Zeiri

*Department of Chemistry, Nuclear Research Center, Negev, P.O. Box 9001, Beer-Sheva, Israel*

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Classical molecular dynamics simulations have been performed to study the details of collision-induced desorption (CID) of nitrogen molecules adsorbed at low coverages on Ru(001). Semiempirical potential energy surfaces (PES) were used to describe the movable two layers of 56 ruthenium metal atoms each, the nitrogen adsorbate, the Ar and Kr colliders, and the interactions between them. An experimentally measured threshold energy for the CID process of 0.5 eV and the dependence of the cross section  $\sigma_{\text{des}}$  on incidence energy and angle of incidence have been precisely reproduced in the energy range of 0.5–2.5 eV. Strong enhancement of the  $\sigma_{\text{des}}$  is predicted as the angle of incidence increases. Kinetic energy and angular distributions of the scattered rare gas and the desorbing nitrogen were determined as a function of the dynamical variables of the collider. It is predicted that half of the collision energy is transferred to the solid and the other half is shared among the two scattered species. While no vibrational excitation is observed, efficient rotational energy excitation is predicted which depends on both incident energy and angle of incidence. Polar and azimuthal angular distributions were found to be strongly dependent on the incidence angle and energy of the colliders. These results suggest a new CID mechanism for the weakly chemisorbed nitrogen molecules on Ru(001), based on extensive analysis of individual trajectories. According to this mechanism, the CID event is driven by an impact excitation of frustrated rotation or tilt motion of the adsorbed molecule as a result of collision with the energetic rare gas atom. In addition, lateral motion along the surface is also excited. Strong coupling of these two modes with the motion in the direction normal and away from the surface eventually leads to desorption and completes the CID process. The efficiency of this coupling is dictated by the details of the corrugation of the Ru–N<sub>2</sub> PES. It is concluded that the simple hard cube–hard sphere model, frequently used to analyze CID processes, is insufficient for the description of this system. While reasonably well predicting threshold energy, it cannot explain the full dynamical picture of the CID event. © 1999 American Institute of Physics. [S0021-9606(99)71206-7]

## I. INTRODUCTION

Industrial high pressure and temperature conditions expose adsorbates on solid surfaces to collisions with gas atoms and molecules which have sufficient kinetic energy to induce dissociation or desorption.<sup>1–8</sup> At the low kinetic energy regime, these collision-induced reactions are possible via a strong chemisorption of gas phase molecule which induces the desorption or dissociation of preadsorbed species in a process identified as adsorption assisted desorption.<sup>8–11</sup> In order to eliminate the effect of the new surface bonding formation on the desorption or dissociation of the adsorbate, a rare gas collider replaces the reactive gas in model experimental and theoretical simulations of the collision-induced events. This enables one to define and characterize the pure gas-adsorbate collision dynamics and its role in the collision-induced reactivity of adsorbates.

Here we have limited ourselves to the simplest collision-induced process which leads to desorption—CID. The first quantitative description has been a theoretical one by Zeiri *et al.*,<sup>2</sup> who investigated the CID of Xe on Si by energetic Xe

from the gas phase. It was then followed by similar studies of the CID of N<sub>2</sub> and Ar from W(100).<sup>3,12</sup> Experimentally, the CID process has been demonstrated and characterized for the first time by Ceyer and co-workers, who studied the CID of weakly bound CH<sub>4</sub> on Ni(111).<sup>4</sup> Classical trajectory analysis based on a hard cube model<sup>13</sup> has emphasized the dominance of direct impact collisions on the outcome of reactive CID events with highest probability for small impact parameter collisions. A more recent work by Levis and co-workers has focused on the ability to extract binding energy of an adsorbate from the threshold energy for CID. This has been demonstrated for the CID of NH<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> from Pt(111).<sup>6,14</sup> The CID cross sections of these molecules being more strongly bound (chemisorbed) are orders of magnitude lower than those measured for CH<sub>4</sub> on Ni(111) at comparable incident kinetic energies of colliders. These studies were based on the hard cube model analysis,<sup>15</sup> estimating an effective surface mass as a fitting parameter.<sup>16</sup> The CID of adsorbed Xe on Pt(111) has recently been investigated following collisions with energetic Ar.<sup>8</sup> In this study molecular

dynamics simulations were used to examine and analyze the experimental data, concluding that for this system, at zero coverage limit, the dynamics can be well understood by the simple hard sphere–hard cube model. A unique enhancement of CID at grazing angles of incidence has been reported for the  $\text{O}_2/\text{Ag}(001)$  system. For off-normal incidence the cross section for CID was found to be 40 times larger than that for the normal incidence collision geometry. The strong coupling of the adsorbate  $x$ – $y$  motion on the surface with its motion along the  $z$  direction mediated by the surface corrugation, was suggested as an explanation for this observation.<sup>17(a)</sup> Finally, desorption and dissociation of  $\text{O}_2$  from  $\text{Pt}(111)$  following energetic Xe collisions were very recently reported as well.<sup>17(b)</sup>

The present work provides details on molecular dynamics (MD) simulations of the CID process of  $\text{N}_2$  from  $\text{Ru}(001)$ . This system was recently investigated experimentally and the results have been presented in a previous publication.<sup>18</sup> The  $\text{N}_2/\text{Ru}(001)$  system has been very well defined by various surface characterization tools, e.g., low-energy electron diffraction,<sup>19</sup> high-resolution electron-energy-loss spectroscopy (HREELS),<sup>19–22</sup> as well as work function and temperature programmed desorption (TPD).<sup>23</sup> Nitrogen interaction with ruthenium is a particularly interesting model system because of its high efficiency as a non-iron ammonia synthesis catalyst.<sup>24</sup> The nitrogen molecule is adsorbed perpendicular to the surface at an on-top site.<sup>19</sup> An ordered  $\sqrt{3} \times \sqrt{3} R30^\circ$  overlayer is formed at  $\Theta(\text{nitrogen}) = \text{N}_2/\text{Ru} = 0.33$ , but the coverage can almost be doubled at adsorption temperature below 85 K.<sup>19</sup> Two TPD peaks are detected following adsorption temperature below 85 K. These seem to arise from two different adsorbed species due to their quite different effect on the system work function.<sup>19,23</sup> The low temperature species has been suggested to originate from laying down molecules formed at higher coverages,<sup>19</sup> but there is no agreement on this assumption.<sup>20</sup>

## II. MD CALCULATIONS

The simulations were performed using the stochastic classical trajectory approach.<sup>2,25</sup> The surface was represented by a slab having two layers of movable Ru atoms which were attached to two additional layers clamped to their lattice positions. Two movable layers have been verified to be sufficient for a reliable description of energy exchange between the collider and the substrate.<sup>2</sup> Each one of the movable and the fixed layers were composed of  $7 \times 8 = 56$  metal atoms arranged to represent the  $\text{Ru}(001)$  surface. Periodic boundary conditions were imposed in the directions parallel to the surface ( $X$  and  $Y$ ). The interaction of the slab with deeper layers of the crystal was represented by 56 fictitious particles<sup>2,3</sup> coupled to the second layer atoms along the  $Z$  direction (normal to the surface).

The adsorbed  $\text{N}_2$  molecule was positioned at the center of the slab. Once the adsorbate was positioned on the slab, each atom was assigned an initial velocity. The initial velocities were sampled from a Boltzmann distribution at the surface temperature, fixed in all simulations at 90 K. After the

initial positions and velocities of the slab atoms and the adsorbate were defined, a standard thermalization procedure was employed to obtain the initial conditions for each trajectory.<sup>2,8</sup>

Following the thermalization, a collider (Ar or Kr) was introduced. Its initial position was fixed at a normal distance from the surface of  $\approx 10$  Å. The lateral position of the collider was fixed according to its predefined incidence polar and azimuthal angles with respect to a random point on the surface near the location of the adsorbate. The collider's initial velocity was assigned according to the magnitude of its kinetic energy examined.

The parameters varied in the different calculations include the initial collider kinetic energy and its incidence angles (polar and azimuthal). For each set of parameters, 1000–10 000 trajectories were calculated. A trajectory was terminated if one of the following conditions was fulfilled:

- (1) A predefined maximum number of integration steps,  $N_{\text{max}}$ , was reached. In the first set of simulations we assigned  $N_{\text{max}} = 2000$ , however, due to relatively small normal velocity of some desorbates not all CID events were accounted for. Hence, the results described below correspond to  $N_{\text{max}} = 10\,000$ . Since the time step used was 1 fs, the above values of  $N_{\text{max}}$  correspond to 2 and 10 ps, respectively.
- (2) Desorption of the adsorbate was recorded.

The quality of the simulations of systems such as the one described in the present work depends on the accuracy of the potential energy surfaces (PES) used. In order to achieve quantitative agreement between the calculation and the experiment, a reliable PES should be employed. In the following sections we shall describe the semiempirical potential functions used to represent the various interactions in the system.

### A. Interaction among metal atoms

The interaction among the slab (movable) atoms has been described by a model due to Head-Gordon and co-workers,<sup>26</sup> and assumed to be harmonic. It was demonstrated there that harmonic interaction between nearest-neighbor (n.n.) and next-nearest-neighbor (nnn) Ru atoms provides an accurate representation of the  $\text{Ru}(001)$  surface.

### B. Collider–substrate interaction

The interaction between the collider rare gas atom and the  $\text{Ru}(001)$  surface was described by a pairwise sum of two-body potentials. Also in this case we have followed Head-Gordon and co-workers<sup>26</sup> and represent the Ar–Ru pair interaction as a truncated Morse potential. This PES was proven to reproduce accurately the results of adsorption experiments by Menzel and co-workers.<sup>26</sup> For the case where Kr was the collider, the equilibrium distance from the surface was increased from 3.8 Å (Ar–Ru) to 4.3 Å (Kr–Ru).

TABLE I. Parameters used to evaluate the PES for the Ar, Kr/N<sub>2</sub>/Ru(001) system.

| Interacting pair                     |                                                    |                                                 |                                |
|--------------------------------------|----------------------------------------------------|-------------------------------------------------|--------------------------------|
| Ar-N                                 | $\epsilon_{\text{Ar-N}} = 6.827 \times 10^{-3}$ eV | $\sigma_{\text{Ar-N}} = 3.252$ Å                |                                |
| Kr-N                                 | $\epsilon_{\text{Kr-N}} = 8.534 \times 10^{-3}$ eV | $\sigma_{\text{Kr-N}} = 3.685$ Å                |                                |
| N-N                                  | $D_{\text{N-N}} = 9.773$ eV                        | $\beta_{\text{N-N}} = 2.670$ Å <sup>-1</sup>    | $R_{e,\text{N-N}} = 1.10$ Å    |
| Ru( <i>i</i> )-N <sub>2</sub> (c.m.) | $D_{i\text{-c.m.}} = 7.2395 \times 10^{-2}$ eV     | $\beta_{i\text{-c.m.}} = 2.500$ Å <sup>-1</sup> | $R_{e,i\text{-c.m.}} = 3.20$ Å |

### C. Collider-adsorbate interaction

The Ar-N<sub>2</sub> interaction was represented by a sum of pairwise potentials between the rare gas atom and each of the nitrogen atoms. The pair interaction was represented by Lennard-Jones (LJ) potentials,

$$V(R_{\text{Ar-N}}) = 4\epsilon_{\text{Ar-N}} \left[ \left( \frac{\sigma_{\text{Ar-N}}}{R_{\text{Ar-N}}} \right)^{12} - \left( \frac{\sigma_{\text{Ar-N}}}{R_{\text{Ar-N}}} \right)^6 \right]. \quad (1)$$

The parameters in Eq. (1),  $\epsilon$  and  $\sigma$ , were chosen such that Ar-N<sub>2</sub> scattering data in the gas phase could be reproduced.<sup>3,27</sup> The values of  $\epsilon$  and  $\sigma$  used in the simulations are shown in Table I for both Ar and Kr, the Kr values were estimated from comparison of gas phase interactions to gas-surface data.<sup>27(c)</sup>

### D. Adsorbate-substrate interaction

Billing *et al.*<sup>28</sup> developed a semiempirical PES for the interaction of nitrogen with Re(001). This PES reproduces the available experimental data for this system. The experimental data for the N<sub>2</sub>/Ru(001) system, related to vibrational frequencies and binding energies of molecular adsorption, are quite similar to those of N<sub>2</sub>/Re(001). The main difference between the two systems is that the dissociation probability of nitrogen on the Re(001) surface<sup>29</sup> is an order of magnitude larger than the corresponding value on Ru(001).<sup>22,30,31</sup> Thus, the PES for N<sub>2</sub>/Re(001) included a dissociative channel and assumed that the lowest energy molecular adsorption geometry is with the molecular axis parallel to the surface.<sup>28</sup> This molecular adsorption geometry was chosen since it is assumed to be the transition state for dissociative adsorption. In the present study dissociative adsorption was not included due to its negligible probability for nitrogen on Ru(001).<sup>22,30,31</sup> However, it is well established that the molecular adsorption of nitrogen on Ru(001) is with the molecular axis normal to the surface.<sup>19-21</sup> Thus, the following form modeled the adsorbate-substrate PES in the present study:

$$V(\text{N}_2\text{-surf}) = V_{\text{Morse}}(\text{N}_2) + f(\theta) \sum_{i=1}^N V_{\text{Morse}}(R_{i\text{-c.m.}}), \quad (2)$$

where  $R_{i\text{-c.m.}}$  represents the distance from the *i*th surface atom to the position of the molecular center of mass and *N* is the number of surface atoms in the simulation (*N*=56). The N-N and the Ru-N<sub>2</sub>(c.m.) interactions were represented by Morse functions:

$$V_{\text{Morse}}(\text{N}_2) = D_{\text{NN}} (1 - e^{-\beta_{\text{NN}}(R_{\text{NN}} - R_{e,\text{NN}})})^2, \quad (3a)$$

$$V_{\text{Morse}}(R_{i\text{-c.m.}}) = D_{i\text{-c.m.}} (1 - e^{-\beta_{i\text{-c.m.}}(R_{i\text{-c.m.}} - R_{e,i\text{-c.m.}})})^2. \quad (3b)$$

The Morse parameters for the nitrogen-Ru(001) potential, Eq. (3b), were designed to reproduce the experimental binding energy, N<sub>2</sub> center of mass to metal distance and N<sub>2</sub>-surface vibrational frequency of the system.<sup>19-21</sup> The values of the parameters of Eqs. (3a) and (3b) used in the present study are shown in Table I. The term  $f(\theta)$  in Eq. (2) ensured that the largest N<sub>2</sub>-Ru(001) binding energy is obtained at normal molecular adsorption geometry (choosing  $A_{\text{theta}} = 1.1$ , so that a ratio of 1:10 is obtained between the adsorption energy in the normal adsorption configuration compared to the energy of the laying down configuration. The value of  $A_{\text{theta}}$  does not affect the results of the CID dynamics). The functional form used

$$f(\theta) = \frac{(A_{\text{theta}} - 1) + \cos^2 \theta}{A_{\text{theta}}}, \quad (4)$$

where  $\theta$  represents the angle between the molecular axis and the surface normal. It should be noted that if parallel adsorption geometry is required the  $\cos^2 \theta$  term in Eq. (4) should be replaced by  $\sin^2 \theta$ . For most of the simulations described below normal adsorption geometry was used to mimic the N<sub>2</sub>/Ru(001) system. In a small number of calculations the parallel adsorption geometry was assumed in order to examine the influence of the adsorption geometry on the CID process. These situations may represent systems such as O<sub>2</sub> adsorbed on transition metals.

The N<sub>2</sub>/Ru(001) interaction potential for normal adsorption geometry, which had been verified by HREELS and IR measurements,<sup>19</sup> is shown in Fig. 1 as a contour plot of a two-dimensional cut parallel to the surface. The distance between the N<sub>2</sub> center of mass and the surface was fixed here at  $Z_{\text{c.m.}} = 2.8$  Å, which is the equilibrium separation. The threefold symmetry of the adsorption site is clearly seen. The functional form chosen to represent the adsorbate-surface interaction results in adsorption sites located at the threefold hollow sites on the surface (Fig. 1, site A through all calculations), while high energy barriers are obtained at the on-top site. This is in contrast to the experimental evidence which suggests that the N<sub>2</sub> adsorbs to the on-top sites on the Ru(001) surface.<sup>19-21</sup> To correct this discrepancy one has to formulate the adsorbate-surface interaction with a much more complicated potential function (as compared to the one used here). Since the proper symmetry of the PES is obtained using the functional form described above, it was used in all calculations discussed below. It is realized that this approximation may introduce some minor inaccuracies in the description of energy transfer between the adsorbate and the solid atoms.

The energy barriers associated with the adsorbate motion along various pathways parallel to the solid surface are pre-

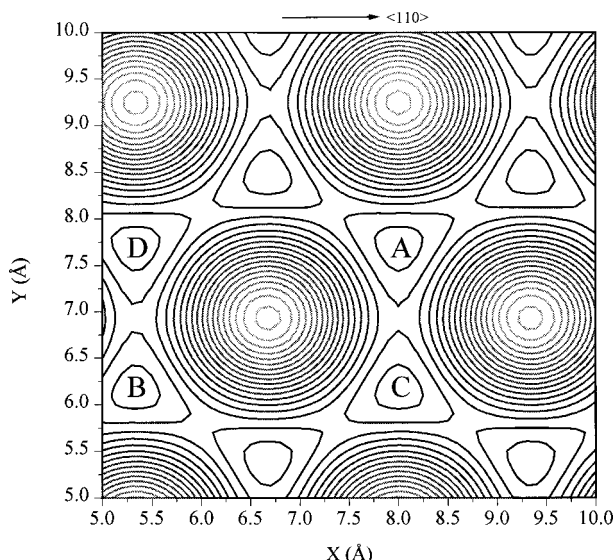


FIG. 1. Contour plot of the adsorbate-substrate PES in a cut parallel to the solid surface. The threefold adsorption sites are marked as A,B,C, and D. See Fig. 2. The contour line spacing is 0.017 eV.

sented in Fig. 2. The reaction path for surface diffusion is between two neighboring threefold sites where the transition state is located at the bridge site. The energy barrier associated with such surface diffusion is about 20 meV. Such a low barrier corresponds to a nearly free motion of the adsorbate between neighboring threefold sites even at low temperatures. The magnitude of the energy barriers along two additional pathways is much larger (in the range 100–250 meV). Thus, the Ru(001) surface is quite flat for motion among neighboring threefold sites but it exhibits a much larger corrugation along other directions.

The PES described above was designed to reproduce most of the available experimental data for the  $N_2$ /Ru(001) system. However, it should be emphasized that it is a semi-empirical model to describe the various interactions in the system.

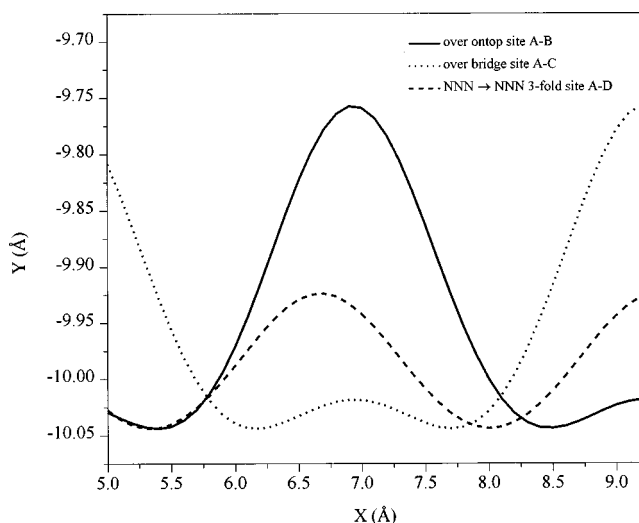


FIG. 2. Diffusion barriers along different directions parallel to the substrate. The potential energy refers to the molecular nitrogen at the gas phase.

### III. RESULTS AND DISCUSSION

The results of the simulations reported below correspond to the low coverage limit studied in the experiment when the interaction among adsorbates can be neglected. Hence, in all the calculations a single adsorbate was used. In the following sections we present results of the calculation and a discussion of the dynamics and mechanism governing the CID process in the following sequence: the cross section for CID, the threshold energy for desorption, the distribution of final kinetic energies of both desorbate and collider, final internal energy distribution, angular distribution of the desorbate and collider. After a summary of the basic results we draw the dominant mechanism of the CID event. The mechanism presented below is supported by thorough inspection of many specific trajectories obtained under various initial conditions.

#### A. Cross section for CID

The basic quantity calculated is the cross section,  $\sigma_{\text{des}}$ , for the CID process. It is computed for a given set of incidence energy, angle of incidence, and adsorption geometry. The cross section for CID is defined as was previously suggested by Beckerle and co-workers<sup>13</sup> as an area on the surface in which an impact of rare gas atom yields a CID event per one adsorbed nitrogen molecule. These cross sections were calculated by numerical integration of the opacity function,<sup>32</sup>

$$\sigma_{\text{des}} = \int_0^{2\pi} d\phi \int_0^{b_{\text{max}}} b P_{\text{des}}(b, \phi) db, \quad (5)$$

where  $\phi$  is the polar angle of the vector connecting the lateral position of the adsorbate c.m. with the position of the predefined impact point on the substrate,  $b$  is the impact parameter (the length of this vector,  $Z$  coordinates of the c.m. and impact point are equal),  $P(b, \phi)$  is the opacity function, and  $b_{\text{max}}$  is the largest impact parameter value beyond which no CID is observed. The opacity function was obtained from the trajectory results.

The results of the simulations describing the variation of  $\sigma_{\text{des}}$  as a function of the incidence energy of the collider,  $E_{\text{in}}$ , at normal incidence ( $\theta_{\text{in}} = 0^\circ$ ) and normal adsorption geometry are presented in Fig. 3. For comparison the experimental results<sup>18</sup> are also shown in Fig. 3. Due to experimental limitations, Ar was used as the collider for  $E_{\text{in}}$  up to 2.25 eV (open triangles) while for larger  $E_{\text{in}}$  values Kr was used (open circles). This data should be compared to the corresponding calculated results with Ar and Kr as collider (closed triangles and circles, respectively). Both experiment and simulation indicate that the CID process has a threshold energy,  $E_{\text{in}} = E_{\text{thr}}$ , below which no desorption is observed. For the  $N_2$ /Ru(001) system both experiment and simulation yield  $E_{\text{thr}} = 0.5$  eV. This value of  $E_{\text{thr}}$  is about twice the magnitude of the adsorbate-surface binding energy. Moreover, both experiment and simulation results indicate that the magnitude of  $E_{\text{thr}}$  is independent of the incidence angle<sup>18</sup> (see the further discussion below in Sec. III B).

Comparison between the experimental and calculated results for  $\sigma_{\text{des}}(E_{\text{in}}, \theta_{\text{in}} = 0^\circ)$  shows an excellent agreement for incidence energies up to  $\sim 3.0$  eV. Above this  $E_{\text{in}}$  value the

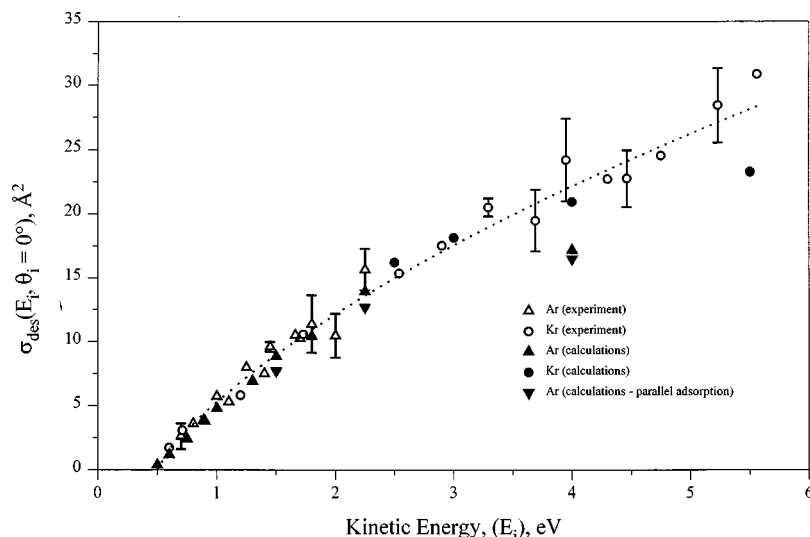


FIG. 3.  $\sigma_{\text{des}}$  as a function of incidence collider energy: experimental (open symbols), calculated for normal adsorption geometry (closed symbols), calculated for parallel adsorption geometry (closed symbols). The dotted line through the experimental data points is based on an expression described in Ref. 18.

increase of the experimental  $\sigma_{\text{des}}$  is faster than the calculated one. This discrepancy is unclear at the moment.

To examine the dependence of  $\sigma_{\text{des}}$  on the adsorption geometry simulations were performed at three  $E_{\text{in}}$  values using parallel adsorption. The calculated  $\sigma_{\text{des}}$ 's for this adsorption geometry are also shown in Fig. 3 as closed inverted triangles. It is clear that in the  $E_{\text{in}}$  range examined here the cross section for CID is independent of the adsorption geometry at  $\theta_{\text{in}} = 0^\circ$ .

Another comparison between experimental and calculated results is shown in Fig. 4. Here, the relationship between  $\sigma_{\text{des}}$  and the collider incidence polar angle (measured from the surface normal),  $\theta_{\text{in}}$ , is presented for four  $E_{\text{in}}$  values. Again, very good agreement between the experimental (open squares) and calculated (closed triangles) data is observed for the case of normal adsorption geometry. For all energy values  $\sigma_{\text{des}}$  exhibits a small increase as a function of  $\theta_{\text{in}}$  up to  $\theta_{\text{in}} = 40^\circ$ . For larger incidence angles a rapid in-

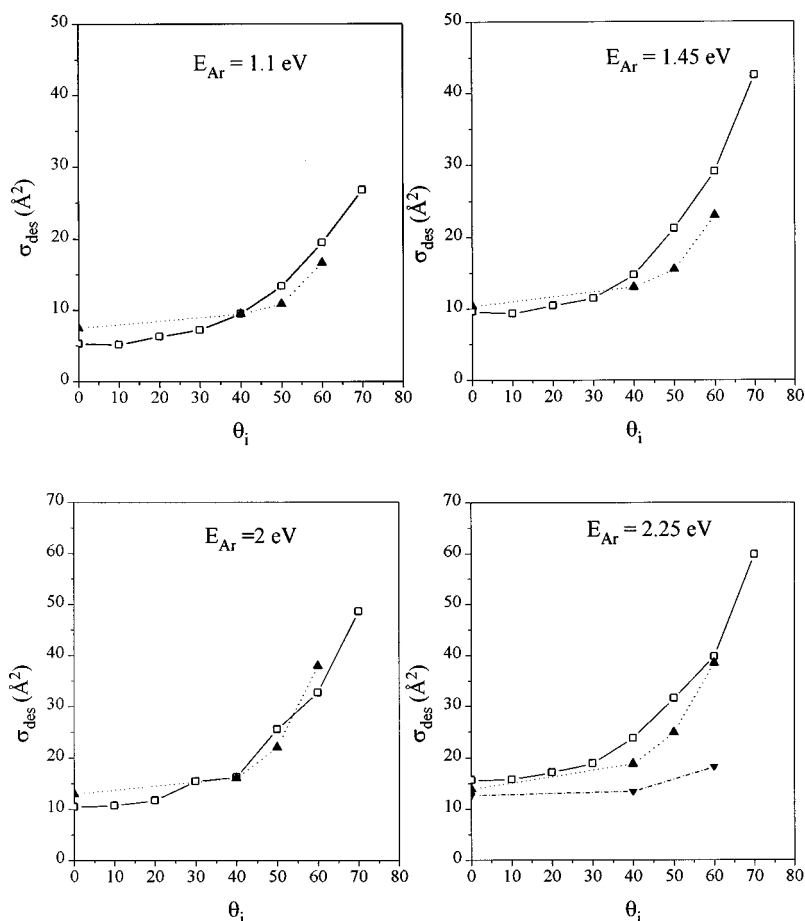


FIG. 4. Experimentally measured (open squares) and calculated (up triangles for normal adsorption geometry and inverted triangles for parallel adsorption)  $\sigma_{\text{des}}$  as a function of incidence angle for four incidence energy values.

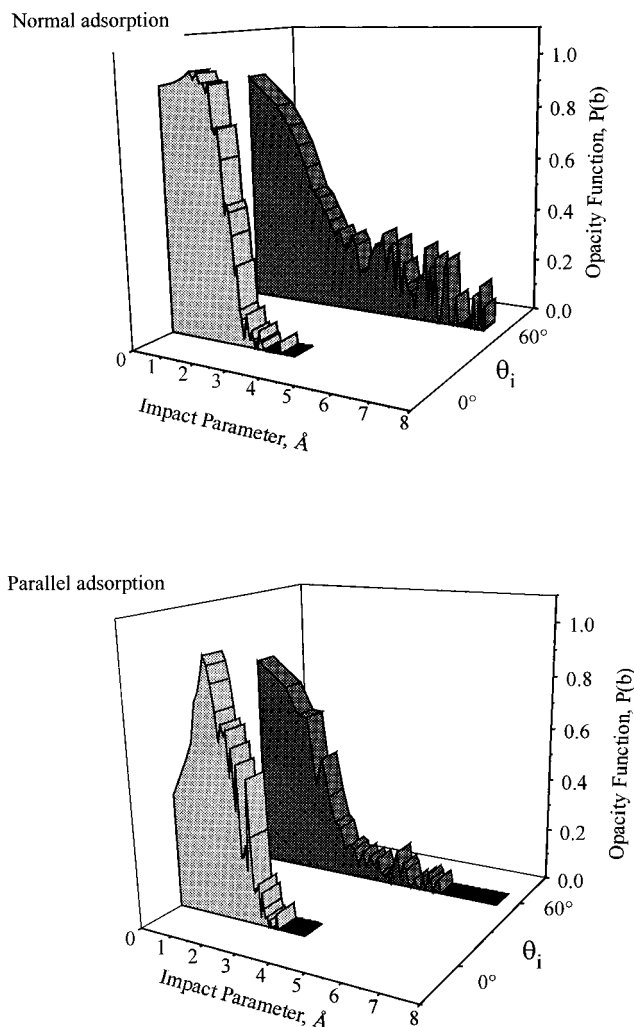


FIG. 5. Opacity function for normal and parallel adsorption at  $E_{in}=2.25$  eV,  $\theta_{in}=0^\circ$  and  $60^\circ$ .

crease in the magnitude of the CID cross section is observed. Calculated cross-section values for  $E_{in}=2.25$  eV using parallel adsorption geometry are also shown for three  $\theta_{in}$  values. It is clear that for off-normal incidence angles the  $\sigma_{des}$  values corresponding to normal adsorption are much larger than those for parallel adsorption. This variation of  $\sigma_{des}$  as a function of the  $\theta_{in}$  is manifested by the changes in the opacity function obtained for different incidence angles. Figure 5 exhibits the variation of  $P_{des}(b)$  as a function of  $b$  (integrated over  $\phi$ ) for two  $\theta_{in}$  values at normal and parallel adsorption geometry. It should be noted that the opacity functions for both normal and parallel adsorption correspond to  $E_{in}=2.25$  eV. For  $\theta_{in}=0^\circ$  at both normal and parallel adsorption  $P_{des}(b)$  exhibits a peak near  $b=1.0$  Å followed by a rapid decay to zero at  $b_{max} \geq 3.0$  Å. The difference between the two adsorption geometries is at near zero  $b$  values. For normal adsorption  $P_{des}(b)$  is close to unity at  $b=0$ , while in the case of parallel adsorption  $P_{des}(b)$  starts at a much lower value. These results suggest that the magnitude of  $b_{max}$  for  $\theta_{in}=0^\circ$  is independent of the adsorption geometry. An increase of  $\theta_{in}$  to  $60^\circ$  results in  $P_{des}(b)$  which maximizes at  $b=0$  Å and decreases monotonically as the impact parameter increases. Here, for both normal and parallel ad-

sorption the opacity function has a low probability tail which extends to large  $b$  values. Comparison of  $P_{des}(b)$  for both adsorption geometries shows that the low intensity tail of  $P_{des}(b)$  for parallel adsorption extends to a smaller  $b_{max}$  value than that for normal adsorption. This difference is attributed to the smaller geometrical cross section “seen” by the collider in the case of parallel adsorption geometry. The geometrical cross section is defined<sup>8</sup> as an area on the surface  $\pi(r_{ads}+r_{gas})^2/\cos\theta_{in}$  in which the gas atom (presented as a hard sphere) impacts the adsorbate (presented as a hard sphere as well). Here,  $r_{ads}$  and  $r_{gas}$  are the van der Waals radii of the adsorbate and gas atom, respectively. The reduced geometrical cross section for parallel adsorption due to its lower profile at the adsorbed state results is much smaller  $\sigma_{des}$  value at  $\theta_{in}=60^\circ$ .

To summarize, the good agreement between the experimental and calculated results indicates that the semiempirical PES used in the simulation allows a reliable description of the Ar/N<sub>2</sub>/Ru(001) system.

## B. Threshold energy for CID

The threshold energy ( $E_{thr}$ ) for desorption is defined as the minimum energy of the collider required to induce desorption. As it follows from this definition,  $E_{thr}$  is closely related to the binding energy of the adsorbate. Levis and co-workers<sup>6,14,16,33,34</sup> proposed a new method to establish the binding energy of an adsorbate based on the experimentally measured threshold energy for desorption. Employing the hard sphere-hard cube (HSHC) model for CID, the binding energy was calculated by the following equation, as suggested by Kulginov and co-workers:<sup>8</sup>

$$E_{binding} = E_{threshold} \frac{4m_{col}m_{ads}}{(m_{col}+m_{ads})^2} \left[ 1 - \frac{4m_{ads}m_M}{(m_{ads}+m_M)^2} \right] \times \cos^4\left(\frac{\theta_{in}}{2}\right), \quad (6)$$

where  $m_{col}$  and  $m_{ads}$  are the collider and adsorbate masses, respectively,  $m_M$  is an effective substrate mass, which is equal to a few times of the mass of a surface atom, and  $\theta_{in}$  is the angle of incidence. Expression (6) yields  $E_{bin}(N_2-Ru) = 0.23$  eV with Ar as the collider and the substrate effective mass is 1.5 times that of Ru atom. This value is in good agreement with our independent measurement of the activation energy for desorption of N<sub>2</sub> from Ru(001) based on TPD line shape analysis. However, it contradicts the value of about 0.4 eV obtained by Menzel and Feulner.<sup>19</sup> To obtain  $E_{bin}=0.4$  eV by Eq. (6) one should substitute  $m_M=6m_{Ru}$  which is thought to be physically meaningless. To further clarify the relationship between the binding energy and the threshold energy for the CID process we increased  $D_{i-c.m.}$  (see Table I) to obtain  $E_{bin}=0.4$  eV and used this modified PES in the MD simulation. The trajectory calculation produced  $E_{thr} \approx 0.85$  eV, which agrees very well with the value calculated from Eq. (6) given  $m_M=1.5m_{Ru}$ , but is 70% higher than the experimental value shown in Fig. 3.

Although the simplified HSHC model provides good agreement with the experimentally measured quantities,

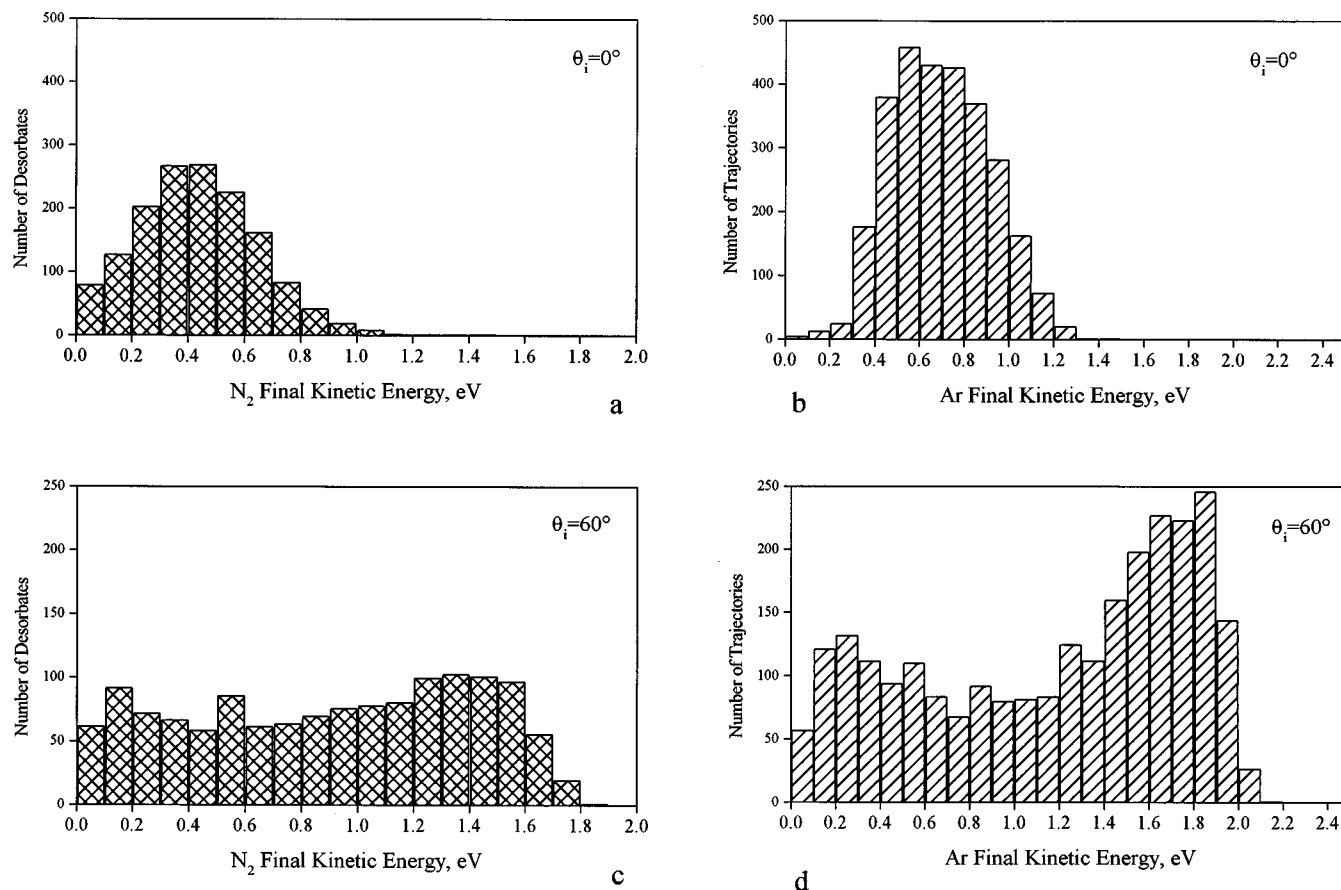


FIG. 6. Final kinetic energy distributions for N<sub>2</sub> (a) and Ar (b) at normal incidence, together with those of N<sub>2</sub> (c) and Ar (d) for  $\theta_{in} = 60^\circ$  at  $E_{in} = 2.25$  eV.

$E_{thr}$  ( $\theta_{in} = 0^\circ$ ) and  $E_{bin}$ , for N<sub>2</sub>/Ru(001) system, assuming the above  $m_M$  value, it cannot explain the experimental observation that  $E_{thr}$  is independent of the angle of incidence.<sup>18</sup> As follows from Eq. (6),  $E_{thr}$  is expected to increase with  $\theta_{in}$ .

The total cross section for CID,  $\sigma_{des}$ , was shown by Beckerle and co-workers<sup>13</sup> to increase with  $\theta_{in}$ . This is due to the faster increase of the geometrical cross section (correlates with  $\cos \theta_{in}$ ), versus the decrease of the normal energy component (correlates with  $\cos^2 \theta_{in}$ ), considered to be relevant for CID within the HSHC model. The magnitude of the increase, however, is far too small to explain the results observed in the N<sub>2</sub>/Ru(001) system. Moreover, the HSHC model predicts the same results for any adsorbed molecule regardless of the specific details of the molecule-metal interaction potential. This is shown to be incorrect in our case where we compare the two model adsorption configurations of N<sub>2</sub>—the normal and the parallel ones. The strong dependence on  $\theta_{in}$  is observed only in the case of the normal adsorption while the parallel geometry reveals practically no dependence on the angle of incidence, as seen in Fig. 4. The limited ability of the HSHC model to treat polar angle dependence of the CID cross section is further demonstrated in the O<sub>2</sub>/Ag(100) system.<sup>17</sup> Here,  $\sigma_{des}$  increases by a factor of 40 as  $\theta_{in}$  increases from normal incidence to  $60^\circ$ . This cannot be explained by any version of the HSHC model.

Since the total threshold energy scaling, as well as  $\sigma_{des}$  enhancement with  $\theta_{in}$  for N<sub>2</sub>/Ru(001) CID (see Sec. III A,

Fig. 4) cannot be explained quantitatively by the HSHC model, we had to reject this approach and rely only on the full three-dimensional MD simulations in the present CID study.

### C. Kinetic energy distributions

Following the impact of the rare gas collider with the adsorbate, it scatters back into the gas phase. The details of the scattering event are dominated by the PES, which describes the interaction among the collider, adsorbate, and the substrate atoms. The amount of energy transferred from the collider to the adsorbate-substrate system depends on the mass ratios, the magnitude of the impact parameter of the rare gas atom with respect to the adsorbate, and the nature of the interaction potentials. The presence of the adsorbate on the surface may be viewed as a source of surface corrugation as seen by the collider. Following the inelastic scattering event, in addition to a change in the collider's translational energy, one also expects changes in its momentum vector which in turn determines its angular distribution.

#### 1. Total energy distributions

Typical kinetic energy distributions,  $\Phi(E_{kin})$ , of Ar (at  $E_{in} = 2.25$  eV) and the desorbed N<sub>2</sub> molecules following a CID event are shown in Fig. 6 for two incidence angles,  $\theta_{in} = 0^\circ$  and  $60^\circ$ . In the case of normal incidence, both desorbed N<sub>2</sub> and Ar exhibit a relatively narrow distribution peaked at 0.4 and 0.6 eV, respectively [Figs. 6(a) and 6(b)].

At low  $b$  values, near head-on collision between the Ar and the adsorbed  $N_2$ , the collider might scatter back to the gas phase with negligible interaction with the substrate. However, in most cases it is deflected by the adsorbate toward the substrate and scatters back to the gas phase following a collision with the surface [see Fig. 14(a), for example]. For large  $b$  values, the collision between the Ar atom and the adsorbate results, in all cases, in a deflection of the rare-gas atom from its initial trajectory followed by its collision with the solid surface [Fig. 14(b)]. Mirror collisions were rarely observed for high  $E_{in}$  and  $\theta_{in}=60^\circ$ . According to the mass ratio of Ar/ $N_2$  the expected energy transfer from the rare gas to the adsorbate is 97% (based on kinematics). On the other hand, in a collision between Ar and the substrate about 65% of the collider normal energy is expected to be transferred to the solid (based on the hard cube model with substrate effective mass of 1.5 the Ru atomic mass). The kinetic energy distribution of the scattered Ar [Fig. 6(b)] indicates that only a negligible fraction of the scattering events correspond to a collision between the Ar and the adsorbate followed by the direct deflection of the collider back to the gas phase (without collider-surface interaction). In most cases the Ar atom interacts with both adsorbate and substrate prior to its return to the gas phase. This is also supported by the kinetic energy distribution of the desorbed  $N_2$  molecules which is peaked at much lower energy than that expected based on kinematic considerations with no surface presented. Detailed analysis of energy transfer processes between the collider and the adsorbate-substrate system is complicated since the Ar- $N_2$  interaction also induces redistribution of the collider energy between normal and parallel motion of the adsorbate. For both species the kinetic energy distributions extend to approximately half of the magnitude of  $E_{in}$  at all incidence energies examined with somewhat less kinetic energy in  $N_2$ .

The desorbate and collider kinetic energy distributions corresponding to off-normal incidence angle exhibit different shapes [Figs. 6(c) and 6(d)]. In this case,  $\Phi(E_{kin})$  for Ar [Fig. 6(d)] is broad and bimodal extending to high energies with peaks at approximately 0.2 and 1.8 eV. A similar bimodal distribution is observed for the desorbates with peaks at 0.2 and near 1.4 eV [Fig. 6(c)]. The analysis of the trajectory results shows that the desorbate high energy peak, and, respectively, low energy peak of Ar stem from the direct collision with small impact parameter ( $0 < b < 2.5$  Å). In contrast to the normal incidence case, here the collider often does not interact directly with the substrate and scatters back to the gas phase after collision with the adsorbate. As the impact parameter increases, the interaction between the adsorbate and the collider becomes weaker, and less energy flows to the desorbate and the CID yield decreases. Side collisions with  $b > 3.5$  Å do not produce desorption. In addition, mirror collisions were rarely observed for high incidence energy.

These variations in the shape of the kinetic energy distributions at off-normal incidence may be rationalized by the following argumentation. The sequence of collisions, i.e., collider-adsorbate and collider-substrate, is expected to depend not only on the magnitude of  $b$  but also on the position of the impact point on the surface,  $R_{im}$ , with respect to the

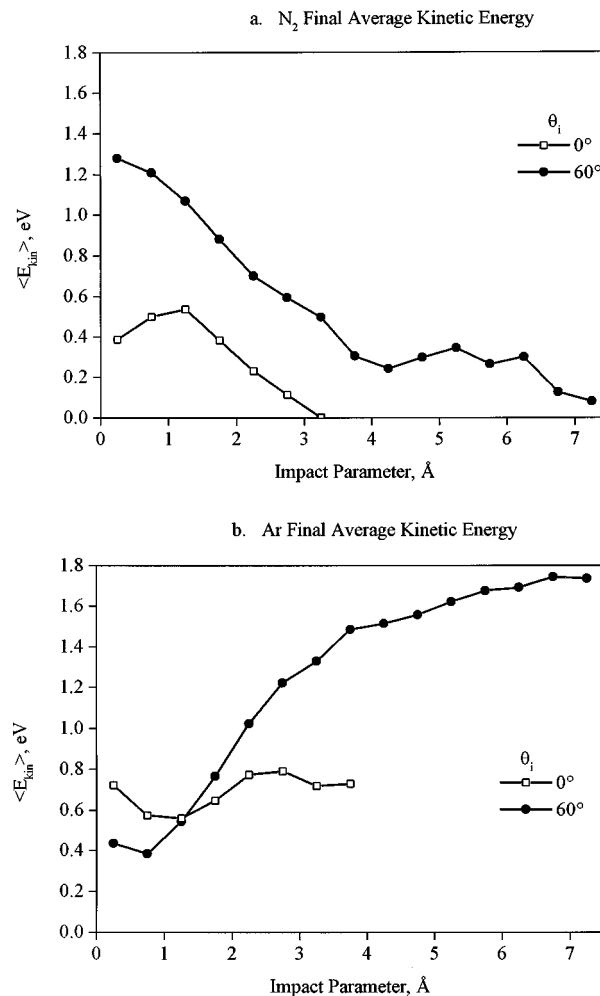


FIG. 7. Distributions of average final kinetic energies of  $N_2$  (a) and Ar (b) as a function of impact parameter.

adsorbate. When  $R_{im}$  is positioned between the adsorbate and the initial position of the collider the rare-gas atom is expected to collide first with the substrate and then, on its way out to the gas phase, with the adsorbate presenting so-called “mirrorlike” collision. A reversed sequence of collisions is expected to occur when  $R_{im}$  is located behind the adsorbate. Moreover, in this case one expects that in many events the collider will be deflected to the gas phase directly after its collision with the adsorbate in a “gliding collision.” The sequence of collisions together with the magnitude of the impact parameter will determine the energy distributions in the system after the scattering event.

## 2. Energy distributions by impact parameter

To illustrate the variation of the kinetic energy distributions as a function of  $b$ , at the two  $\theta_{in}$  values examined, the changes in average kinetic energies,  $\langle E_{kin}(b) \rangle$  for the given impact parameter range are shown in Fig. 7. For normal incidence the  $\langle E_{kin}(b), Ar \rangle$  [Fig. 7(b)] first decreases when  $b$  increases from 0 to  $\sim 1.5$  Å, passes through a minimum, then rises back and levels off, while for the desorbate  $N_2$  the  $\langle E_{kin}(b), N_2 \rangle$  [Fig. 7(a)] exhibits an initial monotonic shift to higher energies as  $b$  increases from 0 to  $\sim 1.5$  Å followed by



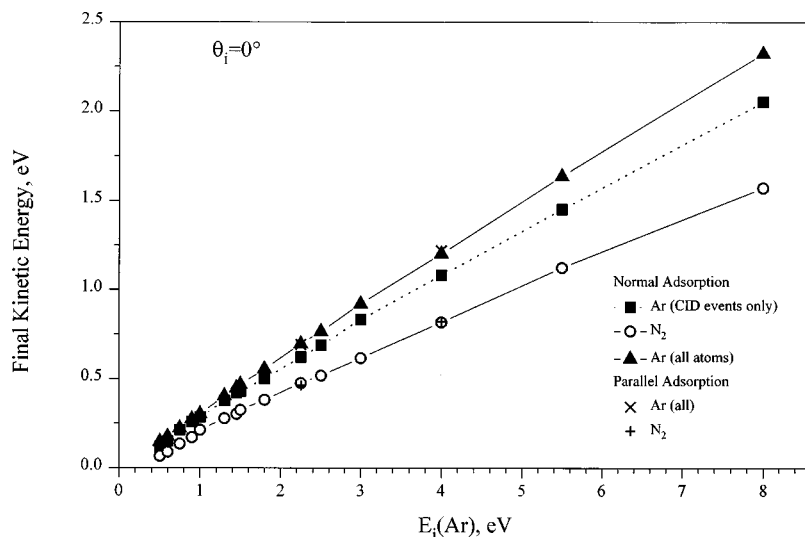


FIG. 8. Variation of  $\langle E_{\text{kin}} \rangle$  as a function of  $E_{\text{in}}$  for normal angle of incidence (desorbates and collider).

a shift to low energies for larger impact parameters. Such behavior is expected since low  $b$  values correspond to strong Ar– $\text{N}_2$  interaction that decreases as the impact parameter increases, however the minimum in  $\langle E_{\text{kin}}(b), \text{Ar} \rangle$  and maximum in  $\langle E_{\text{kin}}(b), \text{N}_2 \rangle$  for the same value of the impact parameter indicates that the most effective collision geometry is not the line of centers at normal incidence. It is interesting to note that CID events at incident energy of the collider near  $E_{\text{thr}}$  and  $\theta_{\text{in}} = 0^\circ$  were obtained at average impact parameter equal to 0.9 Å. This is very similar to the value of 0.7 Å reported at the threshold for CID of Xe from Pt(111) studied by Rettner and co-workers.<sup>8</sup>

The variation of  $\langle E_{\text{kin}}(b) \rangle$  as a function of the impact parameter for off-normal incidence shows a completely different behavior (Fig. 7). Here, small  $b$  values result in a marked excitation of the desorbates leaving the collider with very small energy. Increasing the impact parameter leads to a decrease in the amount of energy transferred from the collider to the desorbate [Fig. 7(a)]. Hence, an increase of  $b$  results in a monotonic decrease of the desorbate energy, while collider energy is shifted to higher energies. These characteristics of  $\langle E_{\text{kin}}(b) \rangle$  for the collider and desorbates are consistent with the discussion above. It should be noted that the  $\langle E_{\text{kin}}(b) \rangle$  for the collider includes both reactive and nonreactive events. Analysis of the data clearly shows that most of the high energy tail in the  $\langle E_{\text{kin}}(b) \rangle$  of Ar corresponds to nonreactive scattering.

The shape of  $\Phi(E_{\text{kin}})$  and  $\Phi(\langle E_{\text{kin}}(b) \rangle)$  was found to be independent of the incidence energy in the range  $0.8 < E_{\text{in}} < 6$  eV. However, these distributions were shifted to higher energies as the magnitude of  $E_{\text{in}}$  increases. In addition, the translational energy distributions obtained in the case of parallel adsorption geometry were very similar to those for normal adsorption (described above). The shift of  $\Phi(E_{\text{kin}})$  as a function of  $E_{\text{in}}$  for the two adsorption geometries examined can be deduced from the variation of the average collider and desorbate kinetic energy,  $\langle E_{\text{kin}} \rangle$ .

### 3. Average final kinetic energy

The dependence of  $\langle E_{\text{kin}} \rangle$  on  $E_{\text{in}}$  for  $\theta_{\text{in}} = 0^\circ$  (integrated over impact parameters) is shown in Fig. 8. In addition to

$\langle E_{\text{kin}}(\text{N}_2) \rangle$  (open circles) and  $\langle E_{\text{kin}}(\text{Ar}) \rangle$  (closed triangles) the average energy of collider following only CID events is also shown (closed squares) as well as the results obtained for parallel adsorption geometry. In the entire  $E_{\text{in}}$  range the average kinetic energy of the desorbates is less than the corresponding values for the collider. It is also clear that events, which do not lead to desorption, result in larger  $\langle E_{\text{kin}}(\text{Ar}) \rangle$ . Comparison of the results obtained for normal and parallel adsorption geometry shows that  $\langle E_{\text{kin}}(\text{N}_2) \rangle$  does not exhibit any marked dependence on the initial adsorbate configuration with respect to the substrate. The variation of  $\langle E_{\text{kin}}(\text{Ar}) \rangle$  with its incidence energy, looks nearly linear within the incidence energy range examined, with a slope of approximately 0.3. In the case of  $\langle E_{\text{kin}}(\text{N}_2) \rangle$  the initial rate of change is approximately 0.25 in the range 0.5–1.5 eV. For larger  $E_{\text{in}}$  values the rate at which  $\langle E_{\text{kin}}(\text{N}_2) \rangle$  changes decreases to approximately 0.18. This change in the rate at which  $\langle E_{\text{kin}}(\text{N}_2) \rangle$  varies is related to an increased energy transfer into the rotational mode of the desorbate (see the discussion below). We note that the sum of the average kinetic and rotational energy of desorbates and collider equals approximately half of the magnitude of  $E_{\text{in}}$ . Hence, in the incidence energy range studied, approximately half of the initial collider energy is channeled into the substrate degrees of freedom. Similar examination of the variation of  $\langle E_{\text{kin}} \rangle$  as a function of  $\theta_{\text{in}}$  shows a nonlinear increase as the incidence angle increases for both desorbates and collider. It is found that up to  $\theta_{\text{in}} = 30^\circ$ ,  $\langle E_{\text{kin}} \rangle$  is practically constant, while for larger incidence angles  $\langle E_{\text{kin}} \rangle$  exhibits a near linear increase. Moreover, the rate at which  $\langle E_{\text{kin}} \rangle$  changes for large  $\theta_{\text{in}}$  increases as a function of  $E_{\text{in}}$ . Again, practically identical behavior was observed for the two adsorption geometries studied.

### D. Internal energy distributions of $\text{N}_2$

The analysis of the internal energy distributions in all the simulations performed did not yield any vibrationally excited desorbates. The energy transferred from the collider to the adsorbate was found to be distributed among the translational and rotational modes only. Typical rotational distribu-

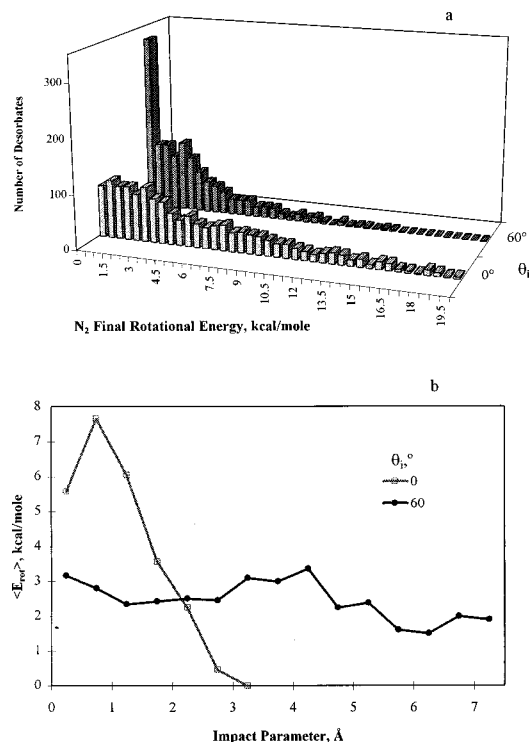


FIG. 9. (a) Rotational energy distribution of desorbates for  $E_{in}=2.25$  eV at normal angle of incidence and  $\theta_{in}=60^\circ$ . (b) Distributions of average final rotational energy of  $N_2$  as a function of impact parameter for both  $\theta_{in}=0^\circ$  and  $60^\circ$  at  $E_{in}=2.25$  eV.

tions,  $\Phi(E_{rot})$ , of the desorbates for  $\theta_{in}=0^\circ$  and  $60^\circ$  at  $E_{in}=2.25$  eV are shown in Fig. 9(a). These results clearly suggest that at normal incidence the energy transferred to the adsorbate is channeled more efficiently into rotational motion than in the case of off-normal incidence. Both distributions exhibit a low energy peak which is followed by a monotonic decrease with long high energy tail. For normal incidence, the high intensity part of  $\Phi(E_{rot})$  is broad and nearly uniform up to  $\sim 4.0$  kcal/mole and the high energy tail extends up to approximately 17 kcal/mole. For  $\theta_{in}=60^\circ$  the distribution is dominated by the peak at  $E_{rot}=0.25$  kcal/mole while the high-energy tail extends only to approximately 10

kcal/mole. Analysis of  $\langle E_{rot}(b) \rangle$  [Fig. 9(b)] for  $\theta_{in}=0^\circ$  shows that for  $b$  in the range 0–1 Å the average rotational energy grows and then rapidly falls down for larger impact parameters,  $b>1$  Å. Similar examination of  $\langle E_{rot}(b) \rangle$  for  $\theta_{in}=60^\circ$  reveals practically constant  $\langle E_{rot}(b) \rangle$ . In all the impact parameter range the tails of the rotational energy distributions extend to much lower maximum  $E_{rot}$  values as compared to the corresponding values in the case of normal incidence.

Similar analysis of  $\Phi(E_{rot})$  for parallel adsorption geometry at the same  $E_{in}$  value shows that the distributions are nearly independent of the incidence angle. Here for both normal and off-normal angles of incidence the rotational distributions are strongly peaked at  $E_{rot}=0.25$  kcal/mole followed by a fast decrease, having a high energy tail up to approximately 12 kcal/mole. These shapes are very similar to those obtained for off-normal incidence angle in the case of normal adsorption geometry.

In order to examine the relation between the desorbate rotational energy and the collider incidence energy we present the dependence of  $\langle E_{rot} \rangle$  on  $E_{in}$  for  $\theta_{in}=0^\circ$  in Fig. 10. A nonlinear relationship between  $\langle E_{rot} \rangle$  and  $E_{in}$  is obtained. At low collider incidence energy (up to approximately 1.0 eV)  $\langle E_{rot} \rangle$  is small and nearly constant, above this value,  $\langle E_{rot} \rangle$  increases more rapidly and reaches a near linear dependence on  $E_{in}$  above 1.5 eV. This nonlinear variation of  $\langle E_{rot} \rangle$  may account for the change in slope of  $\langle E_{kin}(N_2) \rangle$  vs  $E_{in}$  near  $E_{in}=1.5$  eV discussed above. Comparison between the  $\langle E_{rot} \rangle$  values obtained for the two adsorption geometries shows that in the case of parallel adsorption a smaller amount of energy is channeled into the desorbate rotational mode. This difference is related to the CID mechanism of the two adspecies and will be discussed below.

The variation of  $\langle E_{rot} \rangle$  as a function of the incidence angle for five  $E_{in}$  values corresponding to normal adsorption and one to parallel adsorption is shown in Fig. 11. In the case of normal adsorption geometry  $\langle E_{rot} \rangle$  exhibits a linear decrease for increasing values of  $\theta_{in}$ . Again, the rate of  $\langle E_{rot} \rangle$  decrease varies as a function of  $E_{in}$ , namely, larger incidence energy corresponds to a faster decrease of  $\langle E_{rot} \rangle$  as a function of incidence angle. A quite different behavior is ob-

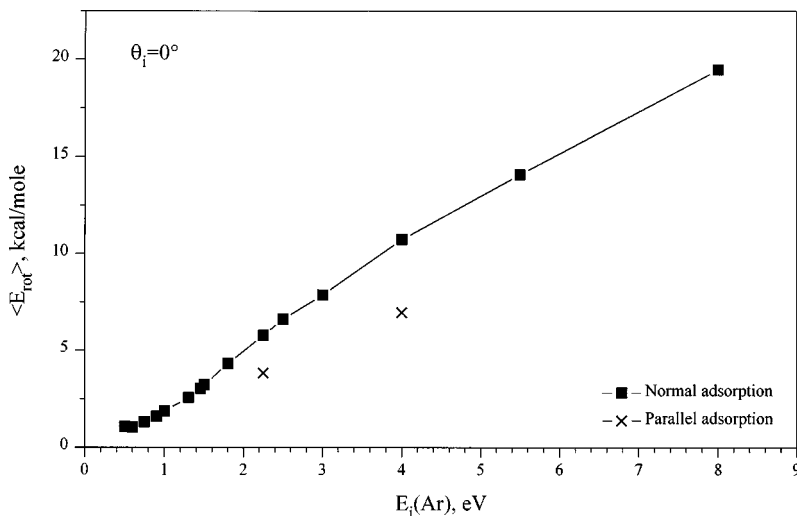


FIG. 10.  $\langle E_{rot} \rangle$  as function of  $E_{in}$  for normal and parallel adsorption at normal incidence.

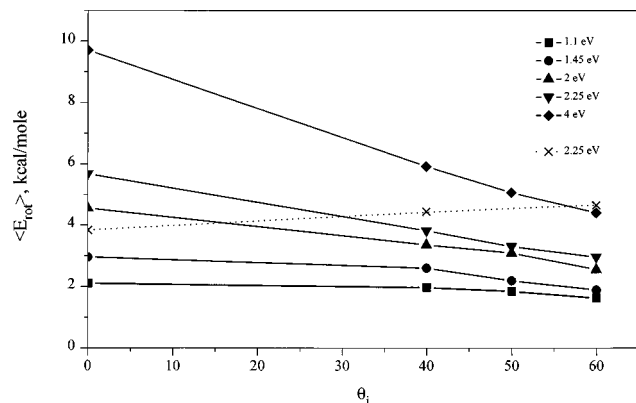


FIG. 11.  $\langle E_{\text{rot}} \rangle$  as a function of  $\theta_{\text{in}}$  for different  $E_{\text{in}}$  values. The parallel adsorption case is shown for comparison (crosses).

served for parallel adsorption geometry. In this case  $\langle E_{\text{rot}} \rangle$  exhibits a slow increase when the incidence angle increases. Thus,  $\langle E_{\text{rot}} \rangle$  at  $\theta_{\text{in}} = 60^\circ$  is larger by about 25% than the corresponding value at  $\theta_{\text{in}} = 0^\circ$ . These characteristics of the dependence of  $\langle E_{\text{rot}} \rangle$  on  $\theta_{\text{in}}$  are closely related to the CID mechanism and will be discussed in Sec. IV.

## E. Angular distributions

### 1. Polar angles

The polar angle distributions,  $\Phi(\theta_{\text{out}})$ , for both collider and desorbates at  $\theta_{\text{in}} = 0^\circ$  and  $60^\circ$  for  $E_{\text{in}} = 2.25$  eV are shown in Fig. 12. In all cases the initial azimuth incidence angle of the collider was chosen to be  $\phi_{\text{in}} = 0^\circ$ , namely, the projection of the velocity vector of the incident particle on the (001) XY plane is directed along the  $\langle 110 \rangle$  crystallographic axis (negative direction of the X axis in Fig. 1). In all simulations a broad distribution was obtained, which covers the entire angular range. For normal incidence the collider distribution [Fig. 12(b)] exhibits broad and nearly constant probability for scattering into the angular range of  $10^\circ < \theta_{\text{out}} < 35^\circ$ . The corresponding  $\Phi(\theta_{\text{out}})$  for the desorbates [Fig. 12(a)] shows a much narrower distribution with a peak centered around  $\theta_{\text{out}} = 60^\circ$ . The distributions for both collider and adsorbate for off-normal incidence angle [Figs. 12(d) and 12(c)] are similar. Here, the distribution is shifted to large scattering angles and the peaks for both collider and desorbate are located near  $\theta_{\text{out}} = 65^\circ - 70^\circ$ . Inspection of the corresponding  $\Phi(\theta_{\text{out}}(b))$  shows that at normal incidence, broad and almost uniform distributions are obtained for 0

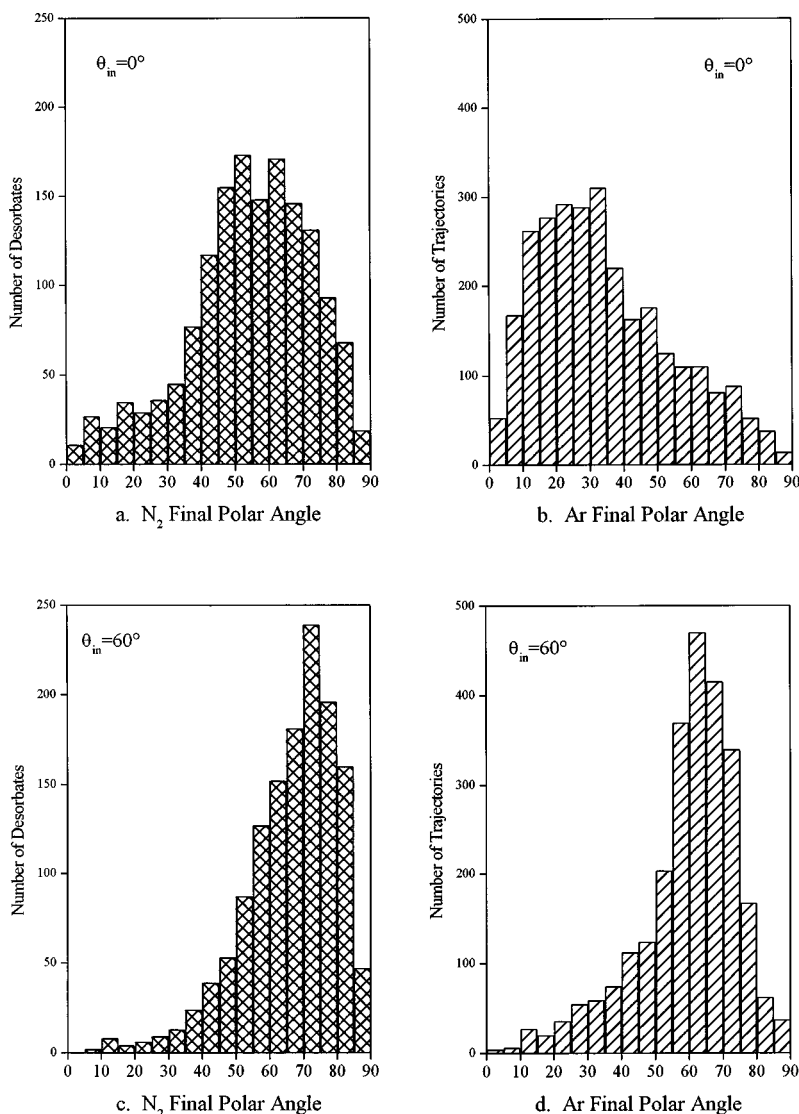


FIG. 12. Polar angular distributions ( $\theta_{\text{out}}$ ) of both Ar and N<sub>2</sub> at  $E_{\text{in}} = 2.25$  eV at  $\theta_{\text{in}} = 0^\circ$  (a), (b) and  $\theta_{\text{in}} = 60^\circ$  (c), (d).

$b < 0.5$  Å for both collider and desorbate. At larger impact parameters, in the range 0.5–1 Å, a peak centered around  $65^\circ$  is observed for both species. Further increase of  $b$  results in a shift of the collider distributions toward low scattering angles with peak centered around consecutively decreasing  $\theta_{\text{out}}$  values. Similarly, the desorbate distributions corresponding to  $b > 1$  Å exhibit a single peak whose center is shifted gradually to larger scattering angles. Since the probability for CID decreases for increasing values of  $b$ , the broad peak observed for the collider in the range  $10^\circ < \theta_{\text{out}} < 35^\circ$  is mainly a result of nonreactive events. In the case of  $\theta_{\text{in}} = 60^\circ$  narrow distributions are obtained for both Ar and  $\text{N}_2$  for the entire impact parameter range. In this case the peaks of all distributions are near  $65^\circ$  independent of  $b$  value. These results indicate that a large fraction of the energy transferred to the adsorbate is converted into desorbate kinetic energy in the directions parallel to the surface. This excitation of the adsorbate translational motion along the surface is related to the mechanism by which the CID process occurs and will be discussed below.

Examination of the polar angle distributions obtained for parallel adsorption geometry shows features similar to those described above. The main difference is that for normal incidence angle the peak of the desorbate distribution  $\Phi(\theta_{\text{out}})$  is located closer to the surface normal, near  $\theta_{\text{out}} = 45^\circ$ . The main contribution to this lower scattering angle is due to CID events with impact parameters in the range 0.5–2 Å. The CID events which correspond to the  $b$  values outside this range lead to broad uniform distributions covering the entire  $\theta_{\text{out}}$  range.

## 2. Azimuthal angles

Here we define the azimuthal angle of the desorbates and colliders after the scattering event as an angle between  $\langle 110 \rangle$  direction (positive direction of the  $X$  axis) and projection of the velocity vector of the projectile on the  $XY$  plane. This differs from the definition of the azimuthal angle of incidence (see Sec. III E 1).

The distributions of the azimuthal angles,  $\Phi(\phi_{\text{out}})$ , of the various species are expected to depend strongly on the incidence polar angle of the collider. For  $\theta_{\text{in}} = 0^\circ$  one would expect a uniform  $\Phi(\phi_{\text{out}})$  while for off-normal incidence angle  $\Phi(\phi_{\text{out}})$  is expected to be much narrower with a peak in the forward direction. The azimuthal angle distribution of the desorbates at normal adsorption geometry for  $E_{\text{in}} = 5.5$  eV at two  $\theta_{\text{in}}$  values are shown in Fig. 13. Indeed, at normal incidence a broad distribution (which spans the whole  $2\pi$  range) is observed, Fig. 13(a). The broad distribution obtained for normal incidence is nonuniform and it exhibits three peaks located near  $\phi_{\text{out}} = 30^\circ$ ,  $150^\circ$ , and  $270^\circ$ . These values correspond to the directions at which the three bridge sites are located around the threefold hollow adsorption site (Fig. 1, site A). Thus, the structure of  $\Phi(\phi_{\text{out}})$  at  $\theta_{\text{in}} = 0^\circ$  reflects the symmetry of the substrate dictated by the corrugation seen by the adsorbate. Similar results were obtained when parallel adsorption geometry was used. Examination of the distribution of the average desorbate kinetic energy as a function of  $\phi_{\text{out}}$  results in a broad distribution with three peaks located at the angles where  $\Phi(\phi_{\text{out}})$  exhibits high in-

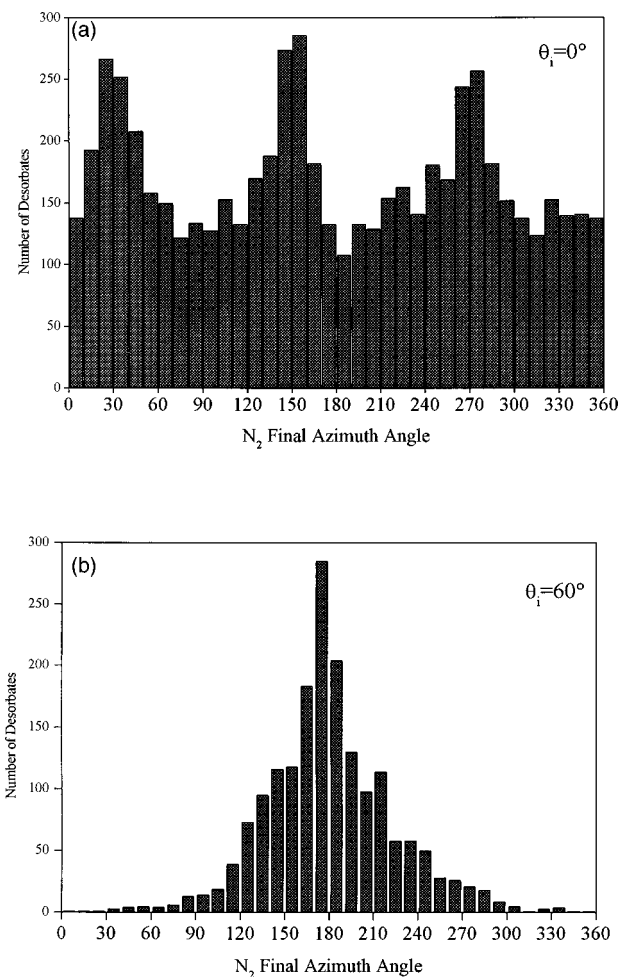


FIG. 13. Azimuthal angular distributions ( $\phi_{\text{out}}$ ) of  $\text{N}_2$  for  $E_{\text{in}} = 5.5$  eV,  $\phi_{\text{in}} = 0^\circ$ , at  $\theta_{\text{in}} = 0^\circ$  (a) and  $60^\circ$  (b).

tensity. This correspondence between the two distributions indicates that the corrugation seen by the adsorbate along the surface has a major role in the successful completion of the CID process.

The  $\Phi(\phi_{\text{out}})$  corresponding to off-normal incidence angle at  $\theta_{\text{in}} = 60^\circ$ , Fig. 13(b), is much narrower with a peak at  $\phi_{\text{out}} = 180^\circ$ . This distribution is expected based on kinematic considerations and due to the symmetry of the substrate. Nearly opposite to this incidence azimuthal angle one finds a bridge site through which the desorbate can penetrate to collide with the substrate atom located behind the bridge site. In most of the events studied this interaction leads to the escape of the adsorbate to the gas phase, see Fig. 1. For incidence azimuthal angles  $\phi_{\text{in}}$  other than along the  $\langle 110 \rangle$  direction the variation of  $\Phi(\phi_{\text{out}})$  should correspond to different corrugation seen by the desorbate on its way to the gas phase. Comparison between  $\Phi(\phi_{\text{out}})$  observed for  $\phi_{\text{in}} = 0^\circ$ ,  $30^\circ$ ,  $90^\circ$ , and  $270^\circ$  (here  $\phi_{\text{in}}$  is defined as in Sec. III E 1) shows that the narrowest distribution corresponds to  $\phi_{\text{in}} = 0^\circ$  and broadest one to  $\phi_{\text{in}} = 30^\circ$ . In all cases the distribution is centered around  $\phi_{\text{out}} = 180^\circ + \phi_{\text{in}}$  as expected from kinematic considerations.

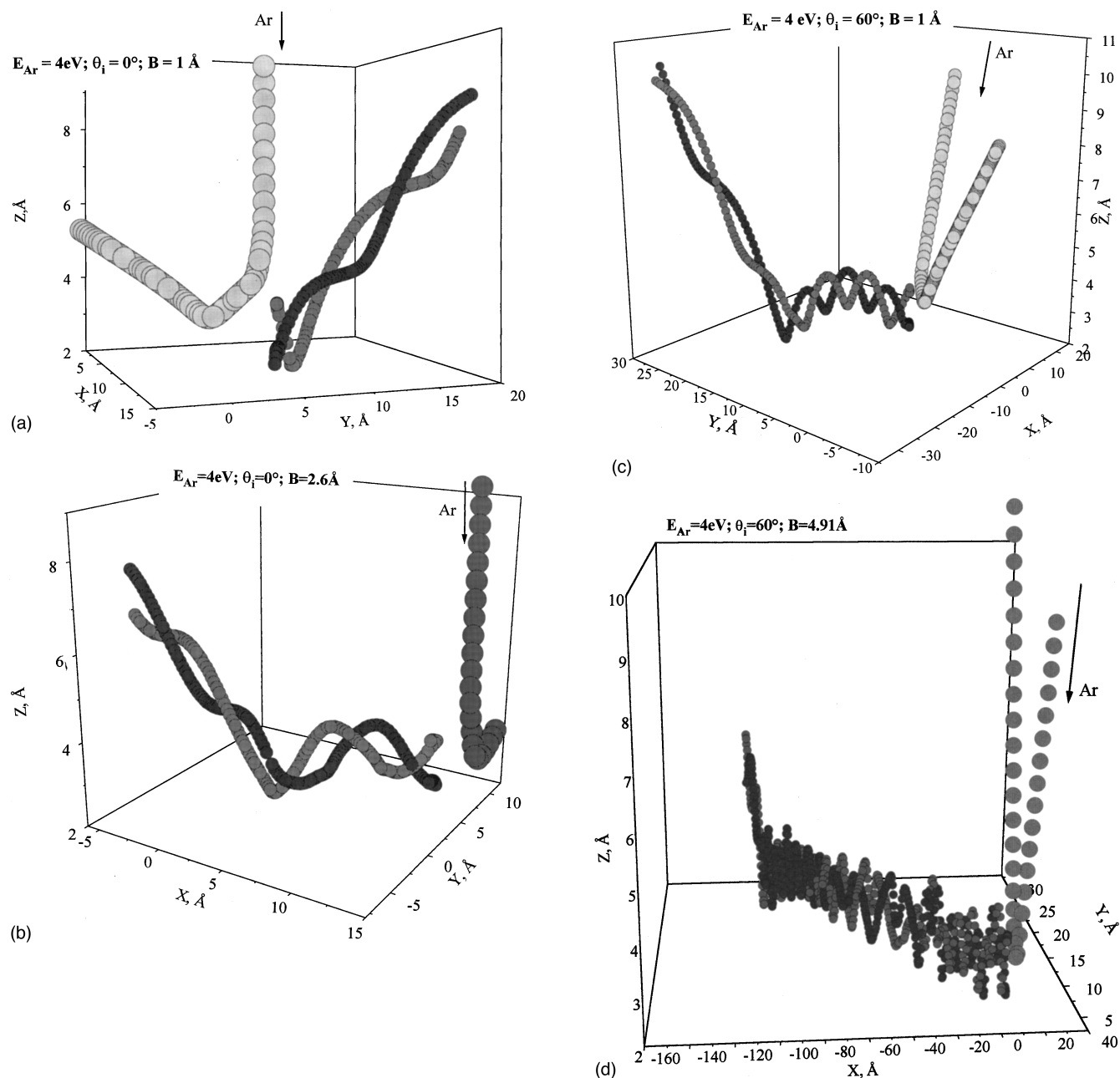


FIG. 14. Four typical trajectories ( $E_{\text{in}}=4$  eV) at  $\theta_{\text{in}}=0^\circ$  and  $60^\circ$ . For  $\theta_{\text{in}}=0^\circ$ ,  $b=1$  and  $2.6$  Å (a), (b), for  $\theta_{\text{in}}=60^\circ$ ,  $b=1$  and  $4.9$  Å (c), (d).

#### IV. CID MECHANISM

To gain insight into the details of the CID mechanism a large number of individual trajectories with different impact parameter values were carefully examined for the energy range  $E_{\text{in}}=0.8$ – $5.5$  eV and both normal and off-normal angle of incidence. Four typical examples for  $E_{\text{in}}=4$  eV are shown in Fig. 14. For each incidence angle a pair of trajectories are shown to illustrate the sequence of events at various  $b$  values that lead to desorption. Note that the  $X, Y, Z$  scales are not identical. For  $\theta_{\text{in}}=0^\circ$  the two trajectories correspond to  $b=1$  and  $2.6$  Å [Figs. 14(a) and 14(b)], respectively. As the projectile approaches the adsorbed nitrogen molecule, the repulsion between the collider and upper N atom rises and causes the molecule to tilt and bend toward

the surface plane approaching a parallel geometry. The adsorbate acquires the largest torque when the collision geometry is not line of centers, but with the impact parameter in the range  $1$ – $1.5$  Å [see Fig. 7(a)]. In this case, the collision between the Ar atom and the adsorbate results in a large amount of energy transferred into the frustrated rotational mode of the adsorbed molecule as well as into translation parallel to the surface [note the large polar angle at which the desorbate leaves the surface,  $\theta_{\text{out}}$  Fig. 12(a)]. Part of the energy in these two modes is transferred into kinetic energy in the direction normal to the substrate, which in turn leads to desorption. The energy transfer into motion along the surface normal is possible due to the coupling of this mode with the frustrated rotation and parallel motion modes by the corrugation of  $\text{N}_2$ –Ru PES. A detailed dynamic picture of the

kind discussed above is of course impossible within the HSHC model, where parallel momentum is assumed constant.

For off-normal incidence the motion of the molecule parallel to the surface prior to its desorption becomes more probable. Figures 14(c) and 14(d) demonstrate the CID events for  $E_{\text{in}}=4$  eV and  $\theta_{\text{in}}=60^\circ$  at two impact parameter values. The parallel momentum transfer from the incoming Ar atom into translational and rotational modes of the adsorbed  $\text{N}_2$  molecule leads to the tumbling of the adsorbate along the surface. This motion is again coupled with the motion normal to the surface by virtue of the PES corrugation.

Thus, the dominant mechanism of the CID is direct impulsive bimolecular collision, in which collider energy is transferred into the frustrated rotation of the adsorbate, its kinetic energy along the surface plane, and into the surface. Although the amount of energy transferred into each of these channels is dictated by the collision geometry, the energy acquired by the adsorbate upon collision is effectively channeled by the corrugated molecule-surface PES into the motion normal to the surface. At normal incidence as a result of significant excitation of the frustrated rotation this degree of freedom is kept by the molecule all the way to the gas phase following desorption. At off-normal incidence the frustrated rotation is less important in the CID sequence, and desorbate leaves the surface rotationally colder. Meanwhile, at off-normal incidence the kinetic energy of the collider more effectively channels into the kinetic energy of the desorbate, and the latter leaves the surface translationally more excited relative to the normal incidence case.

## V. CONCLUSIONS

Classical molecular dynamics simulations have been performed to understand the details of the collision-induced desorption (CID) of very low coverage  $\text{N}_2$  from Ru(001), following collisions of Ar and Kr in the energy range of 0.5–5.5 eV. Semiempirical potential energy surfaces (PES) have been employed to describe the slab of two layers of 56 movable surface atoms and the interactions of the nitrogen molecules with the metal and between the colliders and the adsorbed nitrogen and the metal. These potentials are based on dynamical observables which have been determined experimentally. The computed CID cross sections ( $\sigma_{\text{des}}$ ) based on these PES were found to describe very well the experimentally determined  $\sigma_{\text{des}}$  as a function of incident energy and angle of incidence.

The threshold for CID has been determined at 0.5 eV, which is half of the binding energy of  $\text{N}_2$  to Ru(001), in full agreement with the experimental data. This is used as an independent determination of the adsorption energy of molecular nitrogen of 0.25 eV, erroneously used in the literature as 0.4 eV. Enhancement of the CID cross section at large angles of incidence has been reproduced accurately, revealing a unique CID mechanism. At the same time it rules out the ability to analyze the results on the basis of the simple hard cube–hard sphere (HCHS) model, often used to explain CID processes.

Kinetic energy distributions of the scattered rare-gas atoms following direct collision with the adsorbate and of the desorbing nitrogen molecules were obtained and resolved as a function of the collision impact parameters. These distributions suggest that direct hit of the collider on the adsorbate is the predominant way to lead for CID. Close to half of the initial colliders' kinetic energy is transferred to the solid, almost independent of the incident energy.

Polar and azimuthal angular distributions of the desorbing nitrogen have been calculated. Both are strongly dependent on the colliders' angle of incidence but hardly change with incidence energy. At normal incidence collisions, the azimuthal distribution of the desorbing molecules is predicted to reproduce the substrate hexagonal symmetry.

There is absolutely no vibrational energy excitation of the desorbing  $\text{N}_2$  as a result of the CID process. Rotational excitation, on the other hand, is significant and provides an important insight into the CID mechanism. It increases linearly with incidence kinetic energy, but it decreases as the angle of incidence increases for the same colliders' kinetic energy.

Finally, these observations have led to the following CID mechanism for the weakly chemisorbed  $\text{N}_2$  on Ru(001), with its molecular axis perpendicular to the surface: As a result of the impact between a rare-gas atom and the nitrogen adsorbate, energy is transferred into frustrated rotation or tilt motion of the nitrogen molecule. In addition, translational motion and migration along the surface is also caused by this impact. The coupling between these modes and the motion normal to the surface results in desorption. This coupling is dominated by the PES corrugation.

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