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# FEATURE ARTICLE

## Surface Processes Induced by Collisions

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Energetic gas-phase particles that collide with adsorbed species on solid surfaces induce a variety of processes. Collision induced processes (CIP) are important and may play a central role in the mechanism governing heterogeneous catalytic reactions at high pressures and elevated temperatures. A number of different CIPs are discussed in this article with a strong emphasis on the utilization of molecular dynamics (MD) simulations as a tool for gaining molecular level mechanistic and dynamic insight into chemical events under investigation. Collision induced desorption (CID) is the simplest CIP to be discussed. The CID of  $N_2$  from Ru(001) is described as a test case for the effect of collisions on a polarized adsorbate and has been studied at both low and high coverages. The interpretation of the experimental data at low coverage using MD simulations has led to the introduction of a new desorption mechanism. It involves strong coupling of surface corrugation and adsorbate frustrated rotation that lead to a normal motion away from the surface. Another system for which CID was shown to provide unique information is that of water on Ru(001). Here, the enhanced CID rate was demonstrated to be selective for a specific adsorption site/structure on the surface (the  $A_2$  site). providing a new insight into the structure of water on this surface, recently recalculated by employing ab initio methods. At the multilayer coverage range, a remarkable stability was found of the ice layer against CID, suggesting particularly efficient dissipation of the collider energy within the hydrogen bonded network at an ice thickness of 3 bilayers and above. A unique CIP to be discussed is collision induced migration (CIM), a new phenomenon that has never been considered before. Based on MD simulations, it is shown that CIM may result in migration distances of more than 150 Å at very low coverage, whereas at high coverage, these displacements are shortened significantly. The potential importance of this process for inducing novel catalytic routes on surfaces is discussed. A related example involves MD simulations that address the relation between tracer surface diffusion and the pressure of collider from the gas phase. It is predicted that by increasing the pressure in the range 0-500 atm significant changes in adsorbates surface diffusivity should take place as a result of collision induced migration. Finally, CID within the O<sub>2</sub>/Ag(110) system arising from photodissociation of adsorbed molecular oxygen is described. MD simulations were used to explain the experimentally determined coverage dependent phenomena such as desorption yield and angular distribution of desorbates.

#### 1. Introduction

Surface phenomena induced by the collisions of energetic gas-phase particles with adsorbates on solid surfaces are important for the fundamental understanding of primary processes at the gas-surface interface. Colliders from the gas phase should influence elementary surface processes such as diffusion/ migration, bimolecular reactions and desorption of adsorbed species, if they possess enough kinetic energy. A schematic illustration of the various processes involved in collision induced

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a. DISSOCIATIVE ADSORPTION



b. COLLISION INDUCED PROCESSES



Figure 1. Schematic illustration of the various processes involved in collision induced processes (CIP).

processes (CIP) is shown in Figure 1. CID and CIM are collision induced desorption and migration, respectively. Direct dissociation of molecules striking the surface from the gas phase is an important process that will not be covered in this manuscript, as explained below. The dynamics and mechanism of collision induced events have, therefore, been an active area of research for more than a decade.

Early molecular dynamics (MD) simulations have demonstrated that information on adsorbate-surface interaction potential may be obtained from CID studies.<sup>1</sup> Following these simulations, numerous experimental investigations<sup>2-12</sup> have shown that energy transfer from a fast collider to an adsorbate/ surface system can lead to desorption. It was demonstrated for the first time in the case of Ar CID of CH<sub>4</sub> from Ni(111) by Ceyer and co-workers.3,4 The CID of NH3 and C2H4 from Pt(111) was reported by Levis and co-workers,<sup>5,6</sup> O<sub>2</sub> from Pt(111) by Kasemo et al.,<sup>13</sup> O<sub>2</sub> from Ag(110) by Rocca and co-workers,<sup>10–12</sup> Xe from Pt(111) by Rettner et al.,<sup>8a</sup> Ar from Ar covered Ru(001) by Head-Gordon et al.,<sup>8b</sup> N<sub>2</sub> from Ru(001) by Romm et al.,<sup>9</sup> and water from Ru(001) by Asscher and coworkers.<sup>7</sup> Collision induced dissociation of adsorbed species was reported so far in the case of CH<sub>4</sub> on Ni(111), when energetic Xe atoms striked this surface to produce adsorbed methyl and hydrogen as a competing channel to the CID of methane, Cever et al.14,15 In addition, experiments have demonstrated the possibility for intramolecular, Nuzzo et al.,16 and bimolecular (CO oxidation to  $CO_2$ ), Kasemo et al.,<sup>17</sup> reactions induced by hyperthermal projectiles. Collisions of rare gas atoms on a hydrogen saturated Ni(111) resulted in a collision induced

transition of surface hydrogen into subsurface atoms, as reported by Ceyer and co-workers.  $^{18-20}$ 

The source of high energy colliders with trajectories parallel to the surface may also be surface photodissociation of neighbor adsorbates. Experiments by Polanyi and co-workers,<sup>21,22</sup> Zhu et al.,<sup>23,24</sup> Harrison et al.,<sup>25</sup> Ho and co-workers,<sup>26</sup> and simulations performed by Zeiri<sup>27,28</sup> have all demonstrated that "hot" atoms generated photochemically can lead to CID or dissociation of a neighboring adsorbate. The initial conditions for the projectile-adsorbate scattering event in these systems are dictated by the structure of adsorbates on the surface, therefore, considered to represent localized atomic scattering (LAS).<sup>21,22,28</sup> A variety of numerical simulations, including simple hard cube models,<sup>5,6,8</sup> as well as classical MD simulations,<sup>8,28–34</sup> accompanied these experiments.

Collision induced processes on solid surfaces are interesting because of the attempt made to find correlation between ultrahigh vacuum (UHV) studies and measurements performed at high pressures, which are characteristic of industrial conditions. In particular, activated collision induced processes, which have a reasonable rate only at high pressures, can be modeled in UHV using energetic colliders that represent the high energy tail of a Maxwell–Boltzmann distribution of thermal gas at high temperature and high pressure, thus explaining the so-called pressure gap.<sup>35</sup>

The number of particles striking a surface increases linearly with the gas pressure. However, only a small fraction has high enough kinetic energy to induce the CID processes described above. Based on a thermal distribution at 300 K and one atmosphere, the total flux of particles (argon atoms in this example) colliding with a given site on the surface is F = 2.4 $\times 10^8 \text{ s}^{-1}$ . The number of energetic particles hitting a given site on the surface can be compared with the "turnover number", TN, defined as the number of product molecules produced per unit area (or per catalyst's surface atom) in a unit time. For a heterogeneously catalyzed reaction under typical conditions (e.g., ammonia synthesis) of 400-800 K and up to a few hundred atmospheres of reactant pressure, TN often varies in the range  $10^{-2}$  and  $10^2$  s<sup>-1</sup>.<sup>36</sup> This range of TN is of the same order of magnitude of the number of colliding particles posessing kinetic energy up to 0.7 eV that strike an adsorption site per second (temperature and pressure as described above). Hence, collision induced processes are important routes for obtaining reaction products in heterogeneous catalytic reactions, provided the magnitude of the apparent activation energy associated with the rate determining step is low enough and can be supplied by the projectile. The large value of F suggests that the probability for processes characterized by low activation energies may exhibit nonnegligible dependence on pressure. An example for such a process is surface diffusion of adsorbates. The energy barrier for diffusion  $(E_{diff})$  spans a wide range from close to zero up to about 1 eV, but for many industrially important systems that are catalyzed by metals,  $E_{\text{diff}}$  is in the range 0.15  $\pm$  0.1 eV. Molecular dynamics simulations show that, for such low activation energies, the high collision rate of gas particles on the surface at atmospheric pressure may have a pronounced influence on the diffusion process.37

The purpose of this manuscript is to introduce and discuss a variety of collision induced processes, CIP. The emphasis in the discussion below will be on the detailed mechanism underlying these CIPs. The details of the involved mechanisms will be based on both experimental findings and molecular dynamics simulations of the different events. CID of N<sub>2</sub> from  $Ru(001)^{9,30}$  is an example to be discussed first. Unlike the case

of spherically symmetric adsorbates (e.g., CH<sub>4</sub>), where the CID results can be explained using "hard cube" type models, here, the desorption mechanism, involves a more complicated sequence of steps and energy transfer among different internal modes.

Another system for which CID was shown to provide important information is that of water on Ru(001). In this CID event, selectivity has been demonstrated via an enhanced removal rate of molecules adsorbed at the  $A_2$  (low temperature) sites. This provides a new insight into the unique kinetic isotope effect observed in TPD. In addition, at the multilayer coverage range, an extreme stability against CID of the ice layers is observed at collider energies that are up to an order of magnitude higher than the hydrogen bonding energy. It suggests particularly efficient dissipation of the collider kinetic energy within the hydrogen-bonded network. A sharp onset for this phenomenon is observed at ice thickness of 3–4 bilayers and above.

The N<sub>2</sub>/Ru(001) system has been used, once again, to introduce collision induced migration (CIM),<sup>31</sup> a process that practically does not appear in the literature. The coupling between high gas pressure and surface diffusion was also examined using molecular dynamics simulations.<sup>37</sup> Its correspondence to CIM is discussed.

Finally, quite a different CID mechanism is that of molecular oxygen following photo dissociation of a neighboring oxygen molecule on the Ag(110) surface.<sup>23,24,27</sup> The highly aligned, 2D scattering event between the "hot" photoproduct O atom and the molecular adsorbate will be analyzed in detail.

In this manuscript, we have refrained from any discussion on one of the most extensively studied process of direct collision induced dissociative adsorption (see Figure 1 above). This subject was reviewed in the past<sup>38,39</sup> and has been very successfully covered both experimentally and theoretically via the benchmark system of  $D_2/H_2$  on copper surfaces.<sup>40–43</sup> In addition, other important CIPs that will not be discussed here are Eley–Rideal adsorbate abstraction mechanism<sup>35,44–46</sup> and electron transfer at hyper-thermal energies.<sup>46,47</sup>

#### 2. Collision Induced Desorption (CID)

**2.1.** Ar/N<sub>2</sub>/Ru(001) System. Nitrogen molecules adsorb with their molecular axis perpendicular to the surface, like CO on most metallic surfaces, a geometry that represents an oriented or polarized adsorbed molecule. This is in contrast to the interaction of CH<sub>4</sub> on Ni(111), the CID of which was studied in detail by Ceyer and co-workers,<sup>3,4,14,15</sup> where the molecule can be considered a nonpolarized adsorbate. It will be demonstrated below that the adsorption geometry and the nature of the chemical bond formed on the surface influence significantly the CID mechanism. First, we shall examine the CID process at low N<sub>2</sub> coverage, where experimental data is available, as well as computer simulations considering a single adsorbate on a slab.<sup>9</sup> In the second part of this section, we shall discuss the CID process at high coverage for which no experimental data is available.

2.1.1. CID of Low  $N_2$  Coverage on Ru(001). The cross section,  $\sigma_{des}$ , for the CID process is the basic quantity measured experimentally and calculated in the simulations. It is obtained for a set of incidence energies ( $E_{in}$ ), projectile angle of incidence ( $\theta_{in}$ ), and surface coverages ( $\Theta$ ). The cross section for CID is defined as an area on the surface in which impact of rare gas atom yields a successful CID event for each adsorbed nitrogen molecule. This definition was previously suggested by Beckerle and co-workers.<sup>4</sup> The experimental and theoretical results obtained for normal angle of incident of the collider are



**Figure 2.**  $\sigma_{des}$  as a function of incidence collider energy: experimental (open symbols), calculated for normal adsorption geometry (filled symbols), calculated for parallel adsorption geometry (filled symbols). The dotted line through the experimental data points is based on an expression described in ref 9.

presented in Figure 2. Ar was used as the projectile for collision energy  $(E_{in})$  up to 2.25 eV (open up triangles), whereas for higher energies, Kr seeded in He was used (open circles). These data should be compared with the corresponding calculated results for the same colliders (filled up triangles and circles respectively). Both experiment and simulation indicate that the CID process has a threshold energy,  $E_{in} = E_{thr}$ , below which no desorption is observed. For the N2/Ru(001) system, the threshold was determined to be  $E_{\text{thr}} = 0.5$  eV. This value of  $E_{\rm thr}$  is about twice the magnitude of the adsorbate-surface binding energy. Results of experiments and simulations indicate that the magnitude of  $E_{\text{thr}}$  is independent of the incidence angle,<sup>9</sup> see discussion below. A 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  $\sim$ 2.5 eV. Above this  $E_{\rm in}$  value, the increase of the experimental  $\sigma_{\rm des}$  is faster than the calculated one. To examine the dependence of  $\sigma_{des}$  on the adsorption geometry, simulations were performed at three  $E_{in}$ values using a model, identical binding energy, but parallel adsorption geometry for the N<sub>2</sub> adsorbate.  $\sigma_{des}$ 's calculated for this adsorption geometry are also shown in Figure 2 as filled down triangles. It is clear that in the  $E_{\rm in}$  range examined here the cross section for CID is independent of the adsorption geometry at  $\theta_{in} = 0^{\circ}$ .

Correlation between experimental and calculated results is shown also in Figure 3S (see the Supporting Information) where the relationship between  $\sigma_{des}$  and the collider incidence polar angle (measured from the surface normal),  $\theta_{in}$ , is presented for four different incident kinetic energies. A distinct agreement between the experimental (open squares) and calculated (filled triangles) data is observed for the case of normal adsorption geometry.  $\sigma_{des}$  slightly increases up to  $\theta_{in} = 40^{\circ}$  at all energies. For larger incidence angles, a rapid increase in the magnitude of the CID cross section is observed. Calculated cross sections for  $E_{in} = 2.25$  eV using parallel adsorption geometry are also shown for three angles of incident. It is clear that for off normal incidence angles the cross sections that correspond to normal adsorption are much larger than those for the model parallel adsorption geometry. The agreement level between experimental and calculated results indicates that the semiempirical PES used in the simulation allows a reliable description of the collision dynamics of the Ar/N<sub>2</sub>/Ru(001) system. Details on the potential functions used to describe the projectile-adsorbate, projectilesurface atoms, and interaction among surface atoms including their motion are given elsewhere.9,30

The threshold energy ( $E_{thr}$ ) for desorption is defined as the minimum energy of the collider required to induce desorption. Therefore, from this definition,  $E_{thr}$  is closely related to the binding energy of the adsorbate. Levis and co-workers<sup>5,6,38</sup> proposed a method to extract the binding energy of an adsorbate based on the experimentally measured threshold energy for CID. 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>

$$E_{\text{binding}} = E_{\text{threshold}} \frac{4m_{\text{col}}m_{\text{ads}}}{(m_{\text{col}} + m_{\text{ads}})^2} \left[1 - \frac{4m_{\text{ads}}m_{\text{M}}}{(m_{\text{ads}} + m_{\text{M}})^2}\right] \cos^4\left(\frac{\theta_{\text{in}}}{2}\right) (1)$$

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 metal atom.

The simplified HSHC model provides good agreement with the experimentally measured quantities,  $E_{\text{thr}}$  ( $\theta_{\text{in}} = 0^{\circ}$ ) and adsorbate-substrate binding energy ( $E_{\text{bin}}$ ) for the N<sub>2</sub>/Ru(001) system, assuming  $m_{\text{M}} = 1.5m_{\text{Ru}}$ . However, this model cannot explain the experimental observation that  $E_{\text{thr}}$  is independent of the angle of incidence as was found for the N<sub>2</sub>/Ru(001) system. Moreover, as follows from eq 1,  $E_{\text{thr}}$  is expected to *increase* as  $\theta_{\text{in}}$  increases.

As was shown by Beckerle and co-workers,<sup>3,4</sup> the total cross section for CID,  $\sigma_{des}$ , increases as a function of  $\theta_{in}$ . This behavior was suggested to arise from the faster increase of the geometrical cross section (correlates with  $\cos \theta_{in}$ ) vs the decrease of the normal energy component (correlates with  $\cos^2 \theta_{in}$ ), considered to be the relevant quantity for CID within the HSHC model. The magnitude of the increase, however, is far too small to explain the results observed in the N2/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 prediction is shown to be inconsistent with our model MD simulations for the Ar/ N<sub>2</sub>/Ru system, where the strong dependence on  $\theta_{in}$  is limited to the case of the normal adsorption, whereas the parallel adsorption geometry reveals practically no dependence on the angle of incidence, as shown in Figure 3S (see the Supporting Information). 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>10-12</sup> In this case,  $\sigma_{des}$ increased by a factor of 40 as  $\theta_{in}$  increased from normal incidence to 60°. This cannot be explained by any version of the HSHC model.

More details and deeper understanding can be obtained from further analysis of the MD simulations.<sup>30</sup> Typical kinetic energy distributions of Ar (at  $E_{in} = 2.25 \text{ eV}$ ),  $\Phi(E_{kin})$ , and the desorbed N<sub>2</sub> molecules following CID are shown in Figure 4S (see the Supporting Information) for two angles of incidence,  $\theta_{in} = 0^{\circ}$ and  $60^\circ$  . In the case of normal incidence, both desorbed  $N_2$ and Ar exhibit a relatively narrow distribution peaked at 0.4 and 0.6 eV, respectively (Figure 4S, parts a and b; see the Supporting Information). At low impact parameters (b), near head-on collision, the collider may 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. At larger impact parameters, the collision between the Ar atom and the adsorbate results in deflection of the rare-gas atom from its initial trajectory toward the surface metal atoms. Such "mirror" collisions were rarely observed in trajectories of high  $E_{\rm in}$  and  $\theta_{\rm in} = 60^{\circ}$ . According to the mass ratio of Ar/N<sub>2</sub>, 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  $m_{\rm M}$ =  $1.5m_{\rm Ru}$ ). The kinetic energy distribution of the scattered Ar (Figure 4bS; see the Supporting Information) indicates that only a negligible fraction of the scattering events corresponds to a collision between the Ar and the adsorbate followed by the direct deflection of the collider back to the gas phase (without collidersurface interaction). In most cases, the Ar atom interacts with both adsorbate and substrate prior to its departure back to the gas phase. This is also supported by the kinetic energy distribution of the desorbed N<sub>2</sub> molecules obtained in the MD simulations, which is peaked at much lower energy than that expected based on kinematic considerations with no surface present. A detailed analysis of energy transfer processes between the collider and the adsorbate-substrate system is complicated because the Ar-N<sub>2</sub> 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 associated with N<sub>2</sub>.

The desorbate and collider kinetic energy distributions corresponding to off normal incidence angle exhibit different shapes (Figure 4S, parts c and d; see the Supporting Information). In this case,  $\Phi(E_{kin})$  for Ar (Figure 4dS; see the Supporting Information) 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 (Figure 4cS; see the Supporting Information). An analysis of the trajectories reveals that the desorbate high energy peak and respectively low energy peak of Ar stem from direct collisions at small impact parameter ( $0 \le b \le 2.5$ Å). In contrast to the normal incidence case, here the collider often does not interact directly with the substrate and can scatter back to the gas phase after a 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 > 3.5Å do not lead to desorption.

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,  $R_{\rm im}$ , with respect to the position of the adsorbate. When  $R_{\rm im}$  is positioned at a location that is between the adsorbate and the initial location of the collider, the rare-gas atom is expected to collide first with the substrate and then, on its way back to the gas phase, with the adsorbate exhibiting the so-called "mirrorlike" collision. A reversed sequence of collisions is expected to occur when  $R_{im}$  is located behind the adsorbate (with respect to the initial projectile position). 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". Hence, the sequence of collisions together with the magnitude of the impact parameter will determine the energy distributions in the system after the scattering event.

The variation of  $\langle E_{\rm rot} \rangle$  as a function of angle of incidence for five  $E_{\rm in}$  values corresponding to normal adsorption and one to parallel adsorption are shown in Figure 5S (see the Supporting

Information). In the case of normal adsorption geometry,  $\langle E_{\rm rot} \rangle$  exhibits a linear decrease for increasing values of  $\theta_{\rm in}$ . The rate of  $\langle E_{\rm rot} \rangle$  decrease varies as a function of  $E_{\rm in}$ , namely, larger incidence energy corresponds to a faster decrease of  $\langle E_{\rm rot} \rangle$  as a function of incidence angle. A quite different behavior is observed for parallel adsorption geometry. In this case,  $\langle E_{\rm rot} \rangle$  exhibits a slow increase when the incidence angle increases. Thus,  $\langle E_{\rm rot} \rangle$  at  $\theta_{\rm in} = 60^{\circ}$  is larger by about 25% than the corresponding value at  $\theta_{\rm in} = 0^{\circ}$ . These characteristics of the dependence of  $\langle E_{\rm rot} \rangle$  on  $\theta_{\rm in}$  are closely related to the CID mechanism and will be discussed below.

Finally, we examine the angular distributions of both projectile and desorbates. The polar angle distributions,  $\Phi(\theta_{out})$ , for both collider and desorbates at  $\theta_{in} = 0^{\circ}$  and  $60^{\circ}$  for  $E_{in} =$ 2.25 eV are shown in Figure 6S (see the Supporting Information). These results correspond to the initial collider azimuthal incidence angle of  $\phi_{in} = 0^\circ$ , namely, projection of the velocity vector of the incident particle on the (001) XY plane is directed along the  $\langle \overline{110} \rangle$  crystallographic axis. A broad distribution that covers the entire angular range was obtained in all cases. The collider distribution at normal incidence (Figure 6bS; see the Supporting Information) exhibits broad and nearly constant probability for scattering into the angular range of  $10^{\circ} < \theta_{out}$ < 35°. The corresponding  $\Phi(\theta_{out})$  for desorbates (Figure 6aS; see the Supporting Information) shows a much narrower angular distribution with a peak centered around  $\theta_{out} = 60^{\circ}$ . The distributions at off normal incidence angle (Figure 6S, parts d and c; see the Supporting Information) show similar features. Here, both distributions are shifted to large scattering angles and the peak for both collider and desorbate are located near  $\theta_{\rm out} = 65-70^{\circ}$ . Careful examination of the dependence of the scattering angle on the initial impact parameter,  $\theta_{out}(b)$ , shows that at normal incidence broad and nearly uniform distributions are obtained for both collider and desorbate in the impact parameter range  $0 \le b \le 0.5$  Å. At larger impact parameters,  $0.5 \le b \le 1$  Å, a peak centered around  $65^{\circ}$  is observed for both species. A further increase of b leads to a shift of the collider distributions toward lower scattering angles with a peak located at smaller  $\theta_{out}$  values. Similarly, desorbate distributions corresponding to  $b \ge 1$  Å exhibit a single peak whose center is shifted to larger scattering angles. Because the probability for CID decreases as a function of b, the broad peak observed for the collider in the range  $10^{\circ} < \theta_{out} < 35^{\circ}$  is mainly a result of nonreactive events. In the case of  $\theta_{in} = 60^{\circ}$ , narrow distributions are obtained for both Ar and N2 in the entire impact parameter range. The peaks of all distributions are near 65° independent of b value. This behavior is associated with the large fraction of energy transferred to the adsorbate that 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 the parallel adsorption geometry shows features similar to those described above. The main difference is that for the normal incidence angle the peak in desorbate distribution,  $\Phi(\theta_{out})$ , is located closer to the surface normal near  $\theta_{out} = 45^{\circ}$ . The main contribution to this lower scattering angle is due to CID events with impact parameter in the range 0.5-2 Å. The CID events that correspond to *b* values outside this range lead to broad uniform distributions that cover the entire  $\theta_{out}$  range.

The azimuthal angle of the desorbates and colliders after a scattering event is defined as the angle between the  $\langle 110 \rangle$  direction and the projection of the velocity vector of the particle

on the XY plane. The distributions of the azimuthal angles,  $\Phi$ - $(\phi_{out})$ , of the various species are expected to strongly depend on the incidence polar angle of the collider. For  $\theta_{in} = 0^{\circ}$ , one would expect a uniform  $\Phi(\phi_{out})$ , whereas for an 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 desorbates for  $E_{in} = 5.5$  eV at two  $\theta_{in}$  values are shown in Figure 7S (see the Supporting Information). Indeed, at normal incidence, a broad distribution (which spans the whole  $2\pi$  range) is observed Figure 7aS (see the Supporting Information). However, the distribution is nonuniform, and it exhibits three peaks located near  $\phi_{out} = 30^\circ$ , 150°, and 270°. These values correspond to the directions at which the three bridge sites are located around the 3-fold hollow adsorption site. Thus, the structure of  $\Phi(\phi_{out})$  at  $\theta_{in} = 0^\circ$  clearly reflects the symmetry of the substrate dictated by the corrugation as seen by the adsorbate. Similar results were obtained when parallel adsorption geometry was used.

The  $\Phi(\phi_{out})$  corresponding to off normal incidence angle at  $\theta_{in} = 60^{\circ}$ , Figure 7bS (see the Supporting Information), is much narrower with a peak at  $\phi_{out} = 180^{\circ}$ . Based on kinematic considerations and due to the symmetry of the substrate, this distribution could be expected. For incidence azimuthal angles,  $\phi_{in}$ , other than along the  $\langle 110 \rangle$  direction, the variation of  $\Phi$ - $(\phi_{out})$  should correspond to different corrugation seen by the desorbate on its way to the gas phase. Comparison between  $\Phi(\phi_{out})$  observed for  $\phi_{in} = 0^{\circ}$ , 30°, 90°, and 270° shows that the narrowest distribution corresponds to  $\phi_{in} = 0^{\circ}$  and the broadest one to  $\phi_{in} = 30^{\circ}$ . However, in all cases examined, the distribution is centered, as expected from kinematic considerations, around  $\phi_{out} = 180^{\circ} + \phi_{in}$ .

2.1.2. CID at High N<sub>2</sub> Coverage. The potential functions describing the interaction between projectile-adsorbate, projectile-surface atoms, and surface atoms among themselves including their motion, which were used in the low coverage calculations described in section 2.1.1 above,<sup>9,30</sup> served also for the high coverage simulations. In addition, however, the adsorbate-adsorbate interaction term was introduced. The magnitude of this additional interaction was estimated from the variation of temperature programmed desorption spectra (TPD) as a function of the initial  $N_2$  coverage on Ru(001). These measurements suggest that, at high coverage, the adsorbed species repel each other,<sup>6</sup> a conclusion that is based on the shift to lower temperature of the desorption peak as coverage increases. At full monolayer coverage, the repulsion among adsorbates results in a reduction of the activation energy for desorption by approximately 1 kcal/mol. This repulsion was modeled as a sum of pairwise interactions between nitrogen atoms belonging to different adsorbates. This repulsive N-N pair potential was described by an exponential function of the form

$$V(R_{\rm N-N}) = A_{\rm rep} e^{-\alpha_{\rm rep}R_{\rm N-N}}$$
(2)

The magnitude of the parameters  $A_{\rm rep}$  and  $\alpha_{\rm rep}$  were determined by requiring that the repulsive energy corresponding to a full monolayer of nitrogen molecules will reproduce the experimentally observed reduction in adsorbate—substrate binding. The values of these parameters as used in the simulations were  $A_{\rm rep}$ = 1 eV and  $\alpha_{\rm rep}$  = 0.715 Bohr<sup>-1</sup>. The adsorbate—adsorbate interaction, using eq 2, leads to the necessary decrease of 1 kcal/ mol in the adsorbate—surface binding energy once a monolayer is completed (12 adsorbed molecules on the Ru slab used in the present simulations).



**Figure 8.** Variation of desorption yield as a function of the projectile incidence kinetic energy at the indicated coverages (designated by number of adsorbates,  $N_{ad}$ ).  $N_{ad} = 12$  corresponds to a monolayer coverage.

CID cross sections at low coverage,  $\sigma_{des}$ , were calculated using the opacity function obtained in the molecular dynamics (MD) simulations. The calculation of  $\sigma_{des}$  is meaningful only if there exists an impact parameter value,  $b_{\text{max}}$ , above which the opacity function approaches zero. This requirement was fulfilled in the study of the low coverage limit where a single adsorbate was considered.  $b_{\text{max}}$  depends on the angle of incidence of the projectile, however, but in all cases, its magnitude was larger than 3.5 Å. This value is of the order of the nearest neighbor adsorbate-adsorbate distance at high coverage. As a result, the opacity function is not expected to decrease to zero and cannot be used to calculate the cross section for the CID process at high coverage. Hence, in the present study, efficiency of CID is related to the desorption yield,  $Y_{\rm des}$ , defined by the ratio between the number of desorbates,  $N_{des}$ , obtained in the calculation of  $N_{\text{traj}}$  trajectories (i.e., the number of projectiles considered).

In Figure 8, the variation of  $Y_{des}$  as a function of projectile translational energy at normal incidence is shown for five different coverages. For all coverages, the desorption yield exhibits rapid initial increase as a function of  $E_{in}$ , up to approximately  $E_{in} = 1.75$  eV. At higher energies,  $Y_{des}$  increases less rapidly and tends to converge to a saturation value. The magnitude of  $Y_{des}$  at saturation increases as a function of initial coverage. The increased desorption yields as a function of coverage, for a given incident energy, are due to three main reasons. First, the repulsive interaction among the adsorbates results in a decreased adsorbate-substrate binding. Thus, for a given amount of energy transferred from the collider to an adsorbate, we expect larger desorption probability when coverage increases. Based on the experimental findings, the adsorbate to substrate binding decreases by about 1 kcal/mol when coverage is increased to a full monolayer. As a result of the repulsive energy at the full monolayer, estimated above to be of the order of one kcal/mol, we expect that the threshold energy  $(E_{\text{thresh}})$  for CID at that coverage would be somewhat lower than that obtained in the low coverage limit. Indeed, the results presented in Figure 8 show that  $E_{\text{thresh}}$  for monolayer of adsorbates is smaller by about 10% as compared to the value obtained at low coverage (0.5  $eV^{9,30,31}$ ).

The second reason is that the effective corrugation along the surface felt by an adsorbate increases as a function of coverage. Increase in the potential corrugation leads to a more efficient transfer of adsorbate energy from its translational modes along the surface to the one normal to the surface and, hence, desorption probability increases.

Finally, the probability to obtain multiple desorption events due to the scattering of a single collider increases as a function of projectile kinetic energy, its incidence (polar) angle, and the initial surface coverage. These features are closely related to the desorption mechanism and will be further discussed below.

The response of  $Y_{\text{des}}$  to a change in the incidence polar angle,  $\theta_{\text{in}}$ , at which the collider approaches the surface is interesting for scrutinizing the CID mechanism. These results corresponding to  $E_{\text{in}} = 4 \text{ eV}$  are shown in Figure 9S (see the Supporting Information) for the same five coverages as in Figure 8. It is clear that at the low coverage limit only a very weak dependence of desorption yield on  $\theta_{\text{in}}$  is observed. When off normal angles of incidence are examined,  $Y_{\text{des}}$  increases by a few percent only. It sould be noted that the cross section for CID was found experimentally to increase, in this  $\theta_{\text{in}}$  range, by a factor of approximately four.<sup>9,30,31</sup>

At the low coverage range, variation of  $\theta_{in}$  results mainly in the increase of successful CID events at large impact parameters, but at the same time, a corresponding decrease is found in the yield of CID events at the small impact parameter regime. These two trends almost exactly cancel each other, leading to the observed insensitivity to  $\theta_{in}$ . At the highest coverage, on the other hand,  $Y_{\text{des}}$  increases by 50% when  $\theta_{\text{in}}$  changes from 0° to 60°. Moreover, at monolayer coverage, the desorption yield is larger than unity for  $\theta_{in} = 60^{\circ}$ . In this case a significant fraction of the trajectories end up ejecting more than a single adsorbate. The results shown in Figure 9S clearly demonstrate the nonuniform dependence of  $Y_{des}$  on  $\theta_{in}$  for different initial coverage values. For example,  $Y_{des}$  at monolayer coverage increases by 60% as compared to the corresponding value at low coverage for normal incidence, whereas for  $\theta_{in} = 60^{\circ}$ , the ratio between the desorption yields at monolayer and low coverage increases to 2.5.

Typical translational energy distributions of both desorbates,  $P_{\text{des}}(E_{\text{kin}})$ , and colliders,  $P_{\text{col}}(E_{\text{kin}})$ , for  $E_{\text{in}} = 4 \text{ eV}$  at two values of incidence angle ( $\theta_{in} = 0^{\circ}$  and 60°) are shown in Figure 10S (see the Supporting Information) for the full monolayer case. Inspection of these results shows that both  $P_{des}(E_{kin})$  and  $P_{col}$  $(E_{\rm kin})$  exhibit similar behavior for  $\theta_{\rm in} = 60^\circ$ , a low energy peak followed by a long tail to high energies. In the case of normal incidence, however, these two distributions are markedly different. Another feature that distinguishes between the distributions obtained at the two angles of incidence is the energy range spanned by both  $P_{des}(E_{kin})$  and  $P_{col}(E_{kin})$ . At normal incidence, the highest energy in the distributions corresponds to about half of  $E_{in}$  used, whereas for  $\theta_{in} = 60^{\circ}$ , both  $P_{des}(E_{kin})$ and  $P_{\rm col}(E_{\rm kin})$  extend to much higher energies (i.e., about 80%) of  $E_{in}$ ). These differences can be related to the nature of the projectile collision sequence in each case. At normal incidence, the projectile collides during its approach to the substrate at a relatively large normal distance, with the nearest adsorbate. This collision results in deflection of the collider from its original trajectory to one with an effective off normal incidence angle. However, because most of the projectile translational energy still corresponds to normal motion, it continues its motion toward the turning point. During this part of the trajectory, the projectile may perform additional collisions with one or more adsorbates as well as with the substrate. Once the projectile reached the turning point, it is reflected back to the gas phase. Because the turning point is located at a collider-substrate distance similar to that of the adsorbate-surface distance, the

projectile may suffer additional scattering events before it leaves the solid surface. All of these collision events among the projectile and different adsorbates are expected to occur with a variety of impact parameters. Hence, the amount of energy transferred from the collider to the adsorbates will cover a broad range. Moreover, the interaction between the adsorbates leads to redistribution of transferred energy among the target adsorbates and their neighbors. These effects are clearly demonstrated in the shape of both  $P_{des}(E_{kin})$  and  $P_{col}(E_{kin})$  at normal incidence, see Figure 10S, parts a and b in the Supporting Information).

The sequence of collision events of a projectile at off normal angles of incidence is quite different. In this case, the normal energy component of the collider is much smaller; hence, its turning point corresponds to larger Ar-substrate distances. Similar to the case discussed above, the interaction between the rare-gas atom and the nearest target adsorbate leads to the deflection of the projectile from its original trajectory. If the direction of the projectile normal velocity component is changed, following the deflection, it will proceed to the gas-phase without additional collisions with other adsorbates. Such trajectories can be viewed as a glancing collision of the collider from the adsorbate layer. The amount of energy transferred between the projectile and the target adsorbate is determined by the magnitude of the impact parameter, b. Kinematically, for near zero impact parameter, the projectile may lose up to 90% of its energy to the target N<sub>2</sub>; however, for large impact parameters, the amount of energy transfer becomes much smaller. Although the glancing collisions constitute a small fraction of the trajectories studied, in most cases, the projectile undergoes substantial interaction with a number of adsorbates before it is scattered back to the gas phase. In such trajectories, one expects the collider to lose a large fraction of its initial energy to the adsorbate layer. The adsorbate-adsorbate interaction is expected to result in some degree of energy redistribution among the target adsorbates and their nearest neighbors. As a result, at large incidence, angle collisions are characterized by very broad distributions that span a large energy range and are dominated by a low energy peak as shown in Figure 10S, parts c and d.

Comparison between  $P_{des}(E_{kin})$  and  $P_{col}(E_{kin})$  at high coverage and the corresponding results for low coverage, Figure 4S (see the Supporting Information), shows two main differences: (1) for all of the high coverage distributions, the low energy range is less sensitive to angle of incidence and (2) the high energy peak in  $P_{col}(E_{kin})$  that exists at low coverage is missing in the high coverage distribution. The increased low-energy intensities for high coverage are related to the large probability for multiple collisions (gas-adsorbate and adsorbate-adsorbate) during the CID process. These collisions lead to a more efficient distribution of  $E_{in}$  among the projectile and the adsorbate layer; hence, both collider and desorbates exhibit lower translational energy. The high energy peak in  $P_{col}(E_{kin})$  for low coverage is dominated by large impact parameter collisions where the projectile is reflected back to the gas phase mainly due to its interaction with the substrate. Most of these trajectories do not lead to successful CID events. The absence of a high-energy peak in the high coverage case is related to the fact that the projectile is reflected to the gas-phase from the adsorbate layer and in most CID events does not undergo a substantial interaction with the substrate.

We shall consider now the angular distributions of collider and desorbate in the case of high coverage. The distributions of the polar angles for collider and desorbates at monolayer coverage for  $E_{in} = 4 \text{ eV}$  and two angles of incidence are shown in Figure 11S (see the Supporting Information). A comparison between these distributions and those observed at low coverage, Figure 6S (see the Supporting Information), shows that projectile distributions (Figures 11S, parts b and d; see the Supporting Information) are basically independent of coverage for both incidence angles. In both coverage regimes,  $\Phi(\theta_{out})$  exhibits peaks centered at 25° and 60° for  $\theta_{in} = 0^\circ$  and 60°, respectively. The high coverage leads only to some broadening of the distributions relative to those obtained at low coverage. When coverage is increased, the main changes observed for the desorbates are manifested by a shift of the distributions to smaller angles (i.e., closer to the surface normal) and by marked broadening. For low coverage, the desorbate distributions exhibit a single peak centered near  $\theta_{out} = 60^{\circ}$  and 75° for normal and off normal incidence angles, respectively (Figure 6S, parts a and c; see the Supporting Information). At the monolayer coverage, the whole distribution is shifted to smaller scattering angles and the peaks are centered near  $\theta_{out} = 40^{\circ}$  and  $50^{\circ}$  for normal and off normal angles of incidence, respectively. This shift of  $\Phi(\theta_{out})$  toward the surface normal at increased coverages is due to a cage effect felt by the desorbate. This effect is a result of the desorbate interaction with its neighbors. Thus, the lateral interaction among adsorbates causes a more efficient transfer of their translational energy from the parallel modes to the normal one. The presence of additional adsorbed particles around the desorbing molecule leads to focusing of the desorbates toward the direction of the surface normal.

Examination of the azimuthal angular distributions at monolayer coverage shows that they are practically identical to those obtained for low coverage, Figure 7S. At normal incidence, the distribution is broad and exhibits clearly three peaks just as those seen in Figure 7S. For off normal incidence, the expected distribution with a single peak in the forward direction is obtained. These findings are surprising, mainly those associated with normal incidence, because one would expect that the three peaks associated with the adsorption site symmetry will be "washed out" by collisions of the desorbate with its neighboring adsorbates. The existence of the three peaks at high coverage indicates that the corrugation of the adsorbate-substrate potential is the dominant feature that determines the shape of the distribution. However, it is expected that the symmetry of the adsorbate-surface corrugation will be masked and disappear for systems where the adsorbate-adsorbate interaction are stronger.

2.1.3. CID Mechanism. The detailed CID mechanism was studied through a large number of individual trajectories with different impact parameters at the energy range  $E_{\rm in} = 0.8-5.5$ eV and at various angles of incidence that were carefully examined. A typical trajectory for  $E_{\rm in} = 4$  eV,  $\theta_{\rm in} = 60^{\circ}$  and impact parameter of 1 Å is shown in Figure 12. 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 impact parameter in the range 1-1.5 Å. Here, the collision between projectile and adsorbate results in significant energy transferred into the frustrated rotational mode of the adsorbed molecule as well as into the translation parallel to the surface (note the large distance parallel to the surface the nitrogen molecule tumbles-travels before it desorbs). Part of the energy in these two modes is transferred into kinetic energy in the direction normal to the substrate that in turn leads to desorption. The energy transfer into motion along the surface normal is possibly due to the coupling of this mode with the frustrated



Figure 12. Trajectory demonstrating the CID mechanism. The Ar energy is 4 eV, and the angle of incidence is  $60^{\circ}$  with an impact parameter of 1.0 Å.

rotation. The normal motion is also coupled to motion parallel to the surface due to the corrugation of the N<sub>2</sub>-Ru PES. A detailed dynamic picture of the kind discussed above is of course impossible within the HSHC model, where parallel momentum is assumed to be conserved. For off normal collisions, the motion of the adsorbed molecules parallel to the surface prior to its desorption becomes more probable. Parallel momentum transfer from the incoming Ar atom into translational and rotational modes of the adsorbed N<sub>2</sub> molecule leads to tumbling of the adsorbate along the surface. This motion is again coupled to the motion normal to the surface by virtue of the PES corrugation. More details are given in refs 30 and 31.

The dominant mechanism that governs the CID of N<sub>2</sub> is, therefore, direct impulsive bimolecular collision, in which collider energy is transferred efficiently 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 one of these channels is dictated by the collision geometry, the energy acquired by the adsorbate upon collision is effectively channeled by the corrugated moleculesurface PES into the motion normal to the surface. At normal incidence the significant excitation of the frustrated rotation leads to desorbates with high rotational excitation. At off normal incidence, the frustrated rotation is less important in the CID sequence, and the desorbate leaves the surface with lower rotational temperature. At off normal incidence, the kinetic energy of collider is transferred more effectively to the desorbate. Hence, the desorbate leaves the surface with larger translational energy than that observed at normal incidence.

**2.2. CID of Water from Ru(001).** *2.2.1. Introduction.* The structure of water molecules on solid surfaces has been the subject of extensive research in recent years because of its importance for elementary steps in electrochemistry, astrochemistry, and its relevance to the biological medium.<sup>7,48–63</sup> An interesting feature in the interaction of water molecules with metal surfaces is that the hydrogen bonding among neighbor adsorbates on the surface and is very similar to the binding energy of the molecule to the metal substrate. This makes the water system a unique model for studying lateral interactions among adsorbates. The possible catalytic role of stratospheric ice particles on the destruction of the ozone layer has stimulated further research on ice particles supported by well-defined



Figure 14. TPD of  $H_2O$  and  $D_2O$  following exposure to Kr atoms at 4.6 eV for the indicated time. Initial coverage was 1 BL, the adsorption temperature was 140 K, and the heating rate was 2 K/s, more detils in ref 64.

surfaces. The specific case of water on Ru(001) received special attention. Unique LEED structure analysis of both H<sub>2</sub>O and D<sub>2</sub>O,<sup>59,60</sup> kinetic isotope effect in TPD,<sup>57</sup> CID studies,<sup>7,64</sup> and very recent DFT calculation<sup>65</sup> all were probing this well-defined system.

The best introduction to the water—ruthenium system can be obtained by an inspection of the TPD spectra of  $H_2O$  and  $D_2O$  from Ru(001), as shown in Figure 13S (see the Supporting Information). The three desorption peaks,  $A_1$  at 215 K,  $A_2$  at 180 K, and C at 160 K, are clearly resolved.  $A_1$  and  $A_2$  peaks are considered part of the first bilayer (BL), in direct contact with the metal. The C state is associated with ice-like 3D clusters on the surface.

2.2.2. CID of  $H_2O$  and  $D_2O$  from Ru(001). TPD spectra are shown in Figure 14, following CID of preadsorbed  $H_2O$  and  $D_2O$  (1BL coverage) on Ru(001) by Kr atoms (seeded in supersonic He beam) at normal incidence, having kinetic energy of 4.6 eV. The results of the CID, as revealed by the post collision TPD spectra in Figure 14, were obtained after exposing the water covered surface to the Kr beam for various periods of time, up to 300 s. We observed that water molecules in the  $A_1$  state (desorption near 215K) are removed at much slower rate than molecules in the  $A_2$  state (desorption near 180K), regardless of the water adsorption temperature (90K or 140K). After exposing the surface to a 4.6 eV Kr beam for more than 60 s in the case of  $H_2O$  and 100 seconds for  $D_2O$  the only populated state that remained on the surface is  $A_1$  and some ice-like clusters desorbing near 155–165 K. The hypothesis that  $A_1$  molecules are thermally populated from the  $A_2$  state during TPD has been the basis for an attempt to explain a unique kinetic isotope effect in desorption of H<sub>2</sub>O and D<sub>2</sub>O from Ru(001),<sup>57</sup> see Figure 13S (see the Supporting Information). Based on a careful LEED study, the structure of the  $A_1$  H<sub>2</sub>O molecules was later suggested by Menzel and coworkers<sup>59</sup> to be composed of stable stripe domains on the surface. This structure could not be observed in the case of D<sub>2</sub>O, for which a uniform overlayer structure was proposed.<sup>59,60</sup>

The results shown in Figure 14 suggest that molecules in the A<sub>1</sub> site may have been populated paralel to the desorption of the A<sub>2</sub> molecules as a competing process. Recent DFT calculations by Feibelman,<sup>65</sup> have indicated that a more stable site such as the A1 can be obtained only as a result of direct binding of a water molecule to an adsorbed OH fragment on the surface. Figure 14 may, therefore, be interpreted as indicating that the A<sub>1</sub> sites are composed of water molecules that are bound to OH (or OD) fragments that were generated by collision induced dissociation of a fraction of the water layer on the surface. In fact, a very similar behavior to that in Figure 14 is obtained when the water layer on Ru(001) is exposed to UV photons at 193 nm (6.4 eV) from an excimer laser.<sup>66</sup> Preadsorption of a small amount of oxygen leads to similar results as well.<sup>66</sup> It was previously shown that 6.4 eV photons led to partial photodissociation of water on Pt(111).

We may conclude that our data do not support the unique structure suggested for the  $A_1$  H<sub>2</sub>O molecules based on LEED study.<sup>59</sup> In this study, stripe domains were proposed to explain the observed LEED. Although the CID process uniformly removes the  $A_2$  molecules, the energetic collisions may also cause the dissociation of a fraction of these molecules. It is not expected, however, to maintain or generate a striped structure of the  $A_1$  molecules. Our CID results are more simply explained by the very recent conclusions made by Feibelman,<sup>66</sup> based on his DFT study, where partial dissociation and the hydrogen bonding between water and OH is the origin of the  $A_1$  molecules. The seemingly absent  $A_1$  peak in normal TPD in the case of  $D_2O$ , see Figure 13S (see the Supporting Information), on the other hand, may arise from lower dissociation probability of  $D_2O$  on Ru(001) than H<sub>2</sub>O.

The cross section for CID as a function of the Kr incident kinetic energy for the two water molecule isotopes was measured. Threshold energies of 3.4 eV for H<sub>2</sub>O and 3.8 eV for D<sub>2</sub>O were found.<sup>7</sup> The higher threshold energy in the case of D<sub>2</sub>O can be attributed to the stronger binding of this isotope to the surface ("standard" zero-point energy arguments), as shown by the higher desorption peak temperature of D<sub>2</sub>O in the A<sub>2</sub> state (180 K for H<sub>2</sub>O, 185 K for D<sub>2</sub>O). Note that the threshold energy for desorption is more than 6 times the binding energy of water to the ruthenium metal (about 0.5 eV binding energy in the A<sub>2</sub> sites). The extremely efficient ability to dissipate the colliders' energy is attributed to the unique hydrogen bonded network within the adsorbed water molecules.

Consistent with the high threshold energy for the CID of water, it was found that the ice-like clusters of  $H_2O$  and  $D_2O$  desorbing near 160 K are practically insensitive to collisions with the energetic rare gases.<sup>64</sup> This is in spite of the fact that the hydrogen bonded particles are thermally less stable than the  $A_2$  state molecules which can be removed by the striking energetic Kr. Collision energies up to 5.0 eV, an order of magnitude higher than the hydrogen-bond energy, do not seem to be sufficient to break these intermolecular bonds. This observation suggests that the hydrogen-bonded network is extremely efficient in dissipating high kinetic energies of rare



**Figure 15.** Removal rate of H<sub>2</sub>O following CID using Kr atoms at 5.5 eV. The rate of removal is expressed in terms of coverage of remaining water molecules ( $\Theta$ ) relative to the initial indicated coverage ( $\Theta_0$ ) vs exposure time to the Kr beam.<sup>64</sup>

gas colliders. The kinetic energy of the collider is apparently absorbed by the many inter- and intramolecular vibrational modes and other soft degrees of freedom within the 3D ice structure.

2.2.3. CID of Thicker Water Layers. CID rates of water as a function of layer thickness on Ru(001), reveals an interesting behavior.<sup>64</sup> In Figure 15, the removal rate is determined by the slope of the curves monitoring the remaining water coverage on the ruthenium surface following collisions with Kr at 5.5 eV, as a function of time of exposure to the Kr beam. The ratio  $\Theta/\Theta_{I}$  defines the water coverage remained after exposure to the beam divided by the initial coverage. It is clearly seen that the removal rate becomes significantly slower as the number of water layers increases. The most significant decrease in the removal rate is found at coverages above 2.5 BL. The initial slopes in Figure 15 decrease by an order of magnitude when the removal rate of the first bilayer is compared with that of the third bilayer. This observation is consistent with the discussion above on the extremely inefficient removal of 3D ice-like clusters by means of CID. It shows that unique stability is gained by these clusters once becoming thicker than about 3BL. This observation suggests special packing/organization of the water molecular network of thick layers.

In a recent study by Witek and Buch,<sup>62</sup> the authors employed classical molecular dynamics (MD) simulations to investigate the structure and energetics of the first layers of water on a model metal surface. The water-water empirical polarizable potential was made to fit the water-ruthenium system. The results indicated that a special rearrangement of the water layers takes place at the 3rd and 4th bilayers. This rearrangment is demonstrated in Figure 16S (see the Supporting Information), as side and top views of the first four bilayers. A lateral shift of the upper two bilayers (3rd and 4th) relative to the layers below may explain how a cage is formed for an adsorbate trapped under the water layers. Such a cage was reported for the first time for nitrogen molecules trapped under water layers on Ru(001).<sup>63,64</sup> The results of the MD simulations suggested also that the 4th bilayer is more stable than the structure pertains to three bilayers or less. These calculations qualitatively support our observation that extra stability is onset at 3 bilayers, as seen in Figure 15. The fact that in these calculations the extra stability is found at the 4th bilayer, whereas in the experiment, it seems that the third bilayer is already more stable and is most probably

within the expected uncertainty of the model calculation based on the unknown water-ruthenium potential energy surface.

Section 2.2 can be summarized as follows: (a) CID measurements of H<sub>2</sub>O and D<sub>2</sub>O at coverages near 1 bilayer reveal strong selectivity for the removal of molecules in the A<sub>2</sub> adsorption sites over those in the A<sub>1</sub> sites and the ice-like C sites. (b) Soft removal rates of thicker ice layers as a result of CID with energetic Kr atoms was then studied as a function of the water layer thickness. Near the completion of the 3rd bilayer, a major stabilization of the molecular network structure occurs, which leads to two concomitant effects: (1) a significant decrease in the CID removal rate of the water layers and (2) Caging of coadsorbed molecules (e.g., N<sub>2</sub>, CCl<sub>4</sub>, and CD<sub>3</sub>Cl), followed by an extremely sharp desorption of the trapped molecules near 165 K. This happens at the onset of amorphous solid water desorption temperature. These effects are discussed in terms of the structure of the first layers, which grow on the surface of Ru(001) single crystal and is consistent with recent model molecular dynamics simulations of such a system.

#### 3. Collision Induced Migration (CIM)

3.1. Introduction. Surface processes generated by energetic collisions such as desorption (CID)<sup>1,3,6,8,9,29,39,63,64</sup> and reaction (CIR)<sup>4,17</sup> have been demonstrated. These processes were considered as possible new routes for surface reactivity in industrial catalysis, where energetic gas-phase molecules in the tail of the Boltzmann distribution can affect the heterogeneous catalytic processes.<sup>1,3,29</sup> With this background, it is surprising to realize that the far more probable and facile process of collision induced migration (CIM) has never been considered neither theoretically nor experimentally. The discussion below is based on a single study that was performed so far to address this topic, based on molecular dynamics simulations.<sup>31</sup> The data correspond to CIM of adsorbed nitrogen molecules on Ru(001) at 90 K following collisions with gas-phase argon atoms. The complimentary study of CID of N<sub>2</sub> from Ru(001) has been discussed above. We define as target adsorbate (TM) the molecule directly hit by the projectile. In all of the simulations, the TM was chosen as the adsorbate positioned closest to the slab center.

3.2. MD Simulations: The Ar/N<sub>2</sub>/Ru(001) System. The average migration distance of the TM is shown in Figure 17 for the increasing impact parameter at  $E_{in} = 1.45 \text{ eV}, \theta_{in} = 0^{\circ}$ , 40°, 60° and the indicated initial coverage values. The average migration distance (AMD) is defined as the distance between the position of the TM at t = 0 and its position after 10 ps, averaged over impact parameters within a given range. The AMD function is obtained for trajectories that were found to be nondesorbing during the 10 ps of the simulation. The results clearly demonstrate that at normal incidence the largest displacement of the TM is obtained at nonzero impact parameter,  $b_{\rm imp} \approx 1$  Å. At this collision geometry, the energy transferred from the projectile to the adsorbate is channeled most effectively into lateral migration of the adsorbate. In contrast, for off normal incidence angles (40° and 60°), trajectories having  $b_{\rm imp} \approx 0$  Å are the most effective to induce long migration distances. A strong dependence of AMD on  $\theta_{in}$  is observed. Migration distances that exceed 70Å at the low coverage range (Figure 17) reflect a remarkable efficiency of the CIM process in this system. One may conclude that the collision induced-diffusing molecules experience a rather weak friction by the under-laying substrate while migrating along the surface.

As the coverage increases, the AMD significantly shortens while the CIM process attenuates. This is a direct consequence



**Figure 17.** Average migration distance (AMD) of the target nitrogen molecule (TM) as a function of the impact parameter for the collision. The incidence energy is 1.45 eV and the angles of incidence are  $\theta_{in} = 0^{\circ}$ , 40° and 60°. The average number of trajectories for each point is 20–70 for impact parameters up to 1.5 Å and it grows to 120–150 for the impact parameter range 1.5–2.5 Å and up to 300 for higher impact parameters.

of the multiple interadsorbates collisions of the TM and its neighbor adsorbates. These collisions block the motion of the TM along the surface and, hence, limit the magnitude of AMD. For all of the incidence angles studied, the AMD decreases by nearly an order of magnitude when the coverage increases from 1 ( $\Theta = 0.12$ ) to 12 ( $\Theta = 0.88$ ) molecules on the slab. To estimate the possibility to observe the CIM process experimentally, one has to integrate the AMD values (IAMD) shown in Figure 17 over the entire impact parameter range. The values of IAMD obtained this way were then calculated for different coverages and as a function of Ar kinetic energy. The results are shown in Figure 18S (see the Supporting Information) for two angles of incidence,  $\theta_{in} = 0^{\circ}$  and  $60^{\circ}$ .

These results indicate that the integrated average migration distance is shorter by approximately a factor of 5 than the largest value of AMD. Moreover, the energy dependence is quite modest as compared to that obtain for the AMD function. The reason for this behavior is that there are many more Ar trajectories at large impact parameters which result in small AMD (see Figure 18S in the Supporting Information) than those with small impact parameters and large AMD. As the collision energy increases, AMD values at small impact parameters increase, but at the same time, the number of trajectories at large impact parameters also increase. The net result is a compensation effect which diminishes the overall efficiency and the energy dependence of the CIM.

The simulations demonstrated that single adsorbed molecule can migrate over 150 Å following collisions at high energies and large angles of incidence. As coverage increases, interadsorbate collisions efficiently quench the migration distance. In addition, at high energies, the competing CID becomes dominant, leaving behind only low energy adsorbates that migrate relatively short distances. This leads to an optimal collision energy for the most efficient CIM process near 2.0 eV. Detailed examination of many trajectories following the collision by the projectile shows that the target molecule migrates for long distances because its normal distance to the substrate increase by more than 0.5 Å above its equilibrium position for duration of about 2-5 ps. During this period, the TM experiences a very small barrier for diffusion. An interesting open question that arises from this study and needs to be addressed in the future is the conceptual similarity and difference between CIM and thermal diffusion.

#### 4. Surface Diffusion under High Gas Pressure

**4.1. Introduction.** The main goal here is to examine the possible effect of collision induced migration, as discussed in section 3, on high-pressure surface phenomena, where energetic colliders from the tail of the Boltzmann distribution may enhance surface diffusion under realistic industrial conditions. In this section, we explore the relation between tracer surface diffusion and the pressure in the gas phase. To carry out this task, we performed molecular dynamics simulations of tracer diffusion in the pressure range of 0-500 atm. The calculations were performed for a model system describing the diffusion of an atom like particle, with mass of 28 amu (e.g., nitrogen molecule), on a Ru(001) like surface. The interaction between the adsorbate and the surface was assumed to be identical to the potential energy surface (PES) used to describe the N<sub>2</sub>/Ru(001) system described in sections 2 and 3 above, <sup>9,30,31</sup>

**4.2. MD Simulation: High-Pressure Effect on Surface Diffusion.** According to the N<sub>2</sub>/Ru(001) PES described above, the adsorbate-substrate binding energy is 0.25 eV. This potential was chosen because it exhibits a low barrier for diffusion,  $E_{\text{diff}} = 0.06 \text{ eV}$ , which allows efficient evaluation of the diffusion coefficient using MD. The gas phase was assumed to be constituted of Ar atoms whose binding energy to the Ru-(001) surface was taken to be De(Ar-S) = 75 meV. The value of De(Ar-S) was varied in the simulations to examine its influence on the diffusion constant, see the discussion below. Further details of the calculations and potential energy surface used are described in ref 37.

The simulations were performed for six sets of parameters characterizing the system. The actual values used to define these six groups are shown in Table 1.

In Table 1,  $T_g$  represents the gas temperature, and the last column describes the nature of gas atom-adsorbate interaction. This quantity describes the binding energy between the Ar and the N<sub>2</sub> like adsorbate for cases 1–3 and 5 and 6. In set 4, the Ar-adsorbate interaction was assumed to be repulsive in order to examine the influence of such interaction on the diffusion coefficient,  $D_{dif}$  (for more details see ref 37). For all six cases examined, the variation of  $D_{dif}$  as a function of substrate temperature in the range of 90–180 K, was found to exhibit



**Figure 19.** Variation of the preexponential factor (bottom panel) and of the barrier for diffusion (top panel) as a function of pressure. The numbers in the legend correspond to the "set number" shown in Table 1, section 4.2.

 TABLE 1: Summary of the Parameters Employed in the Six
 Sets of Simulations

set number	<i>T</i> <sub>g</sub> [K]	De(Ar-S) [meV]	gas—adsorbate interaction [meV]
1	300	75	6.8 attractive
2	500	75	6.8 attractive
3	300	375	6.8 attractive
4	300	375	6.8 repulsive
5	300	600	6.8 attractive
6	300	900	6.8 attractive

Arrhenius behavior. The calculated preexponential factors and the activation energies as a function of pressure are shown in Figure 19.

Inspection of these results shows that the preexponential factor,  $D_0$ , and the activation energy for surface diffusion,  $E_{ac}$ , exhibit noticeable variation as a function of the pressure. The preexponential seems to be independent of  $T_{g}$  and the nature of gas-adsorbate interaction (sets 1, 2, and 4). However, a significant dependence of  $D_0(P)$  on the gas-substrate binding energy is observed. In the case of weak binding, a pressure increase results in a monotonic decrease of both  $D_0$  and  $E_{ac}$ . This behavior can be related to the well-established compensation effect.36 On the other hand, for strong gas-substrate binding,  $D_0(P)$  exhibits a small initial decrease followed by an increase by 60% compared to its value at P = 0. Thus, the compensation effect does not seem to apply at high pressure in this case. This behavior can be rationalized if the distribution of the gas particle residence time near the surface is examined. The residence time distributions at P = 200 atm and  $T_s = 180$ K for weak and strong gas-substrate binding are shown in Figure 20S (see the Supporting Information).

Similar results were obtained for lower surface temperatures. It is clear that, when the gas-substrate binding is weak, most of the gas particles undergo a direct scattering and leave the surface after less than 10 fs. For larger De(Ar-S) values, the gas particles are accelerated toward the surface and their energy loss to the substrate result in a much longer residence time near the solid surface. Hence, for stronger gas-solid binding



Figure 22. Typical trajectories with P = 200 atm, De(Ar–S) = 600 meV (set 5 in Table 1), and temperatures of  $T_S = 90$  K (top panels) and  $T_S = 180$  K (bottom panels).

energies, the high pressure leads to the formation of an adsorbed layer that influences the lateral motion of the tracer adsorbate. The interaction between the nitrogen like adsorbate and the layer of gas particles formed at high pressures leads to an increase in the frequency associated with the adsorbate modes parallel to the surface, as a result of the larger effective corrugation experienced by the adsorbed particle. According to transition state theory, the preexponential is proportional to the magnitude of the frequency associated with the motion along the reaction path.<sup>67</sup> Thus, the increase in adsorbate vibrational frequency in directions parallel to the surface, when a layer of gas particles is formed, leads to an increase in  $D_0(P)$  contrary to the expected variation according to the compensation effect.

For all sets investigated, the numbers calculated for  $D_0(P)$ are compared with their value at P = 0 is up to a factor of 2. The corresponding change of  $E_{ac}(P)$  is by a factor of 2-3. However, the dependence of  $D_{dif}$  on  $E_{ac}$  is exponential while on  $D_0$  it is linear. Hence, it is clear that the changes in the activation energy dominate the gross behavior of  $D_{dif}(P)$ . Inspection of the results in Figure 19 shows that, in all cases studied,  $E_{ac}(P)$  decreases monotonically as P increases. The most significant effect on  $E_{ac}(P)$  is due to variations in the gassubstrate binding energy. Only minor dependence, however, is observed on  $T_g$  and the nature of gas-adsorbate interaction. In the case of weak gas-surface binding,  $E_{ac}(P)$  decreases at P =200 atm to about half of its value at P = 0, whereas for strong binding,  $E_{\rm ac}(P)$  changes to approximately one-third of its value at low pressure. For all cases examined,  $E_{ac}(P)$  exhibits an initial rapid decrease when the pressure increases to 50 atm followed by a slower change at higher pressure. These variations of  $E_{ac}$ -(P) can be rationalized based on our understanding of the diffusion mechanism at high pressures.

A large number of individual trajectories were carefully examined to elucidate the relationship between  $D_{\text{dif}}$  and the pressure. Four typical trajectories at P = 0 and two temperatures are shown in Figure 21S (see the Supporting Information). Similarly, four typical trajectories at P = 200 atm, De(Ar–S) = 600 meV and two temperatures are shown in Figure 22. The trajectories shown correspond to  $T_S = 90$  K (top pair in both Figures 21S and 22) and to  $T_S = 180$  K (bottom pair in both Figures 21S and 22). In all cases, the time evolution of the tracer position along the three Cartesian coordinates is presented. Note the scale differences in the figures of the trajectories shown.

Inspection of the adsorbate motion at P = 0 shows that during most of the trajectory it performs thermal vibrations near its adsorption site. Clearly, the diffusional motion consists of random jumps mainly between nearest neighbor adsorption sites. It is quite clear that increasing surface temperature from 90 to 180 K results in a marked increase in the frequency of jumps among neighboring sites, Figure 21S (see the Supporting Information). In some trajectories (for P = 0), occasional jumps to next nearest neighbor or further apart sites were observed. However, in most cases, the transitions were limited to the nearest neighbor site. A quite different situation is obtained in the case of high pressure (P = 200 atm) and high gas-substrate binding energy, Figure 22. Here, many trajectories were observed that represent jumps to distant sites in addition to short jumps to nearest neighbor sites that are driven by the thermal motion of the substrate. These long distance jumps occur, in most cases, simultaneously with large sudden changes in the magnitude of the adsorbate velocity components.

These differences between low and high-pressure trajectories are associated with the source of energy transferred to the adsorbate that also induces its diffusional motion along the surface. At P = 0, the source of energy is the thermal motion of the substrate atoms. The thermal motion of surface atoms near the adsorbate position may lead to energy transfer whose magnitude is larger than the diffusion barrier. This energy

transfer can induce an adsorbate jump to a neighboring site. The substrate temperature is the dominant feature that determines the frequency at which such events occur, as is clearly seen in Figure 21S. In the case of high pressure, an additional energy source that contributes to the adsorbate motion along the surface is the collision of gas particles. The gas particle motion toward the substrate will be accelerated provided that its interaction potential with the solid contains an attraction term. Upon collision of the projectile with the solid, a fraction of its translational energy will be transferred to the adsorbate/substrate complex. In addition, the collision may result in energy transfer from the collider motion along the surface normal to its motion parallel to the surface. If this energy transfer among the gas particle translational modes is large enough, the particle can get temporarily trapped near the surface. For increased gassubstrate binding energy, the projectile acceleration toward the surface will be larger. Hence, a more extensive energy transfer to the adsorbate/substrate complex as well as an increased degree of kinetic energy mixing among the projectile different modes may take place. This in turn will result in a longer trapping of the gas particle near the surface. This effect is demonstrated by the results presented in Figure 20S (see the Supporting Information). Thus, the increase in the gas-substrate binding energy is expected to lead to two main outcomes: an increase in the amount of energy transferred to the adsorbate/solid system and formation of a denser layer of trapped gas particles near the surface. This analysis may explain the observed decrease of  $E_{ac}$ when pressure increases, Figure 19. A larger pressure corresponds to an increased number of gas particles colliding with the adsorbate/substrate system. Hence, a larger average amount of energy transfer from the projectile gas particle to the adsorbate is expected to take place. This increase of the adsorbate energy leads to a corresponding increase in the frequency and magnitude of jumps performed by the adsorbate during its motion along the surface as seen in Figures 21S and 22. Thus, the effective  $E_{ac}$  sampled by the adsorbate at high pressure is expected to be smaller than that at lower pressures.

The discussion above suggests that at high pressures two opposing effects may influence surface diffusion. The first is an increase in the number of gas particles colliding with the adsorbate/substrate system. This is expected to broaden the distribution of adsorbate displacement obtained in the simulations and thus result in an increase of the calculated diffusion coefficient. The other effect is the formation of a layer of gas particles near the surface due to the trapping of projectiles. Once such a layer is formed, it may restrict the motion of the adsorbate along the surface and, hence, lead to reduced diffusion coefficients. Increase in the gas-substrate binding energy is expected to result in the formation of a denser and less mobile layer of trapped projectiles. This is the behavior observed in the present investigation. Apparently, the increase in pressure and residence time of the gas particles near the surface results in more efficient energy transfer into adsorbate modes corresponding to its motion along the surface. However, the increase of the gas-substrate binding energy results in an increase of the diffusion coefficient when De(Ar-S) is changed in the range 75-600 meV (sets 1, 3, and 5 in Table 1). Further increase in the gas-substrate binding, to 900 meV (set 6), does not lead to a corresponding increase of  $D_{\text{dif}}$ . It is clear from Figure 19 that the diffusion coefficients for sets 5 and 6 are almost identical in the entire pressure range examined. Thus, the interplay between the two effects described above and their role in the determination of the magnitude of the diffusion coefficient are clearly demonstrated by the calculated data.

#### 5. Hot Atom Surface Chemistry

**5.1. Introduction.** The  $O_2$ -metal system has been the subject of extensive experimental and theoretical investigations. For all metallic substrates examined, clear evidence for charge transfer from the substrate to the adsorbate was found. In the case of alkali metals, ejection of exoelectrons was observed upon the dissociative adsorption of O<sub>2</sub>.<sup>68-70</sup> Oxygen was found to adsorb in the form of a charged molecular state on several noble metals. Super-oxide  $(O_2^{-})$  and/or per-oxide  $(O_2^{2-})^{71-80}$  are two of those ionic molecular states. Evidence for charge transfer from the metallic substrate to the molecularly adsorbed oxygen was demonstrated in first-principles electronic structure calculations as well.<sup>81-89</sup> Irradiation of the O<sub>2</sub>/metal system results in two main outcomes: desorption of molecular oxygen or its dissociation to yield adsorbed O atoms.90-96 Both routes are believed to correspond to additional charge transfer from the substrate to the adsorbate.

Different mechanisms were suggested to explain the results of various photoinduced desorption experiments. The first is related to the work of Antoniewicz.97 According to this model, photoexcitation of charge carriers in the substrate leads to a sudden increase of the charge-transfer from the metal to the molecularly adsorbed  $O_2$ . This attachment of a hot electron introduces additional charge-image charge attraction to the adsorbate-surface binding. As a result, concurrent with dissociation, the  $O_2^{2-}$  starts to move inward toward the substrate. Upon quenching, detachment of the hot electron, the adsorbate finds itself on the repulsive wall of the ground adsorbatesurface potential. Hence, the force responsible for the  $O_2$ desorption is expected to be along the direction of the surface normal. Therefore, one expects a strong forward peak in the desorbate angular distribution.<sup>25,26,98,99</sup> A different mechanism was suggested recently by Rettner and Lee44 to explain atomic beam induced desorption of O2 from a Pt surface. Here the driving force for O<sub>2</sub> desorption was assumed to be charge withdraw due to the adsorption of an atom from the beam at a neighboring site. The newly formed neutral O<sub>2</sub> finds itself on the repulsive wall of the O<sub>2</sub>-Pt physisorption potential and is repelled to the gas phase. This is similar to the hot hole mechanism proposed for the desorption of  $O_2$  from Pd(111).<sup>100</sup> The hole induced desorption is also expected to result in a strong forward peak in the desorbate angular distribution. The broad angular distributions observed experimentally were explained by long-range coulomb repulsion between the adsorbed atom and the desorbing molecule.44 Recently, this hole-induced desorption process was subject to a theoretical modeling by Katz et al.<sup>101</sup> The simulations examined in detail the excitation route and possible isotope effects.

A new photoinduced desorption mechanism was proposed to explain the desorption of  $O_2$  from Ag(110).<sup>23,24</sup> According to this mechanism, the photoinduced dissociation of the adsorbed molecular oxygen results in the formation of hot oxygen atoms that move along the surface. The encounter between such a hot photoproduct and an adsorbed  $O_2$  can result in a CID of the molecular adsorbate. The CID following photoinduced dissociation of a neighbor oxygen molecule was also observed in the case of  $O_2$  coadsorption with noble gas atoms on Pt-(111).<sup>25,26,98,99</sup> In both cases, a pronounced off normal peak in the desorbate angular distribution was observed.

**5.2. MD Simulations:** O<sub>2</sub> Photodissociation and CID from Ag(110). The details of this CID process induced by "hot" photoproducts was recently examined using numerical simulations. This study was based on molecular dynamics calculations of a model system representing the  $O^*+O_2/Ag(110)$  system

(where O\* corresponds to a hot oxygen atom). More details on the potential energy surfaces (PES) pertaining to this system are given in ref 27.

Examination of the distance traveled by the "hot" atom until it arrives to its final rest position reveals that this distance is strongly dependent on the photoproduct initial translational energy. The variation of the average distance traveled by oxygen atoms,  $\langle R \rangle$ , and their corresponding average kinetic energy,  $\langle E_{\rm kin} \rangle$ , as a function of time are presented in Figure 23S (see the Supporting Information) for five initial translational energies. Each one of the curves shown was obtained by averaging over 500 trajectories. These results clearly indicate that  $\langle R \rangle$ changes markedly as a function of the initial projectile translational energy,  $E_{in}$ . An order of magnitude increase in  $\langle R \rangle$  is observed when Ein is changed from 0.5 to 3.0 eV. The dissipation of the kinetic energy of the oxygen atom is quite rapid, of the order of 1-2 ps. This rate of energy transfer to the substrate exhibits only a weak dependence on  $E_{in}$ . Following this fast energy relaxation, small oscillations in  $\langle R \rangle$  are observed. These oscillations correspond to the adsorbate frustrated translational motion in the neighborhood of its final adsorption site.

The remarkable increase in the magnitude of  $\langle R \rangle$  as a function of  $E_{in}$  is related to the small diffusion barrier along the  $\langle 110 \rangle$ direction on the Ag(110) surface. The rapid energy dissipation is attributed to the strong interaction between the oxygen atom and the substrate atoms along the  $\langle 100 \rangle$  direction. The trajectory of the projectile along the surface is expected to vary as a function of the orientation of the O<sub>2</sub> molecule prior to its dissociation. Hence, the rate of kinetic energy relaxation is also expected to vary as a function of the initial molecular orientation prior to dissociation. For wider distribution of the parent molecule, one expects that the projectile will experience a more rapid relaxation as compared with a projectile originating from a narrow distribution.

Because the width of the distribution of molecular orientation strongly depends on substrate temperature  $(T_s)$ , the magnitude of  $\langle R \rangle$  for a given  $E_{in}$  is expected to decrease for increasing  $T_s$ . Indeed, it was found that by increasing  $T_s$  from 40 to 90 K  $\langle R \rangle$ decreased by 35% for the same  $E_{in}$ .

The details of the CID event should now be discussed. The experiments demonstrated that an increase of surface coverage from 0.25 to 1 ML is correlated with a 60-fold increase in the CID probability. In addition, the polar angle distribution of desorbed O<sub>2</sub> molecules was found to exhibit two peaks, one at  $\theta = 0^{\circ}$  and the other near  $\theta = 45^{\circ}$  (measured from the surface normal). The peak at  $\theta = 0^{\circ}$  was associated with the hole-induced desorption process,<sup>23,24,44</sup> whereas the off normal peak at  $\theta = 45^{\circ}$  was related to the CID process.<sup>23,24</sup>

MD simulations were performed with the goal to better understand the experimental observations and attempt to reveal the microscopic details of the CID process. Both O<sub>2</sub> and atomic oxygen are known to adsorb onto the 4-fold sites along the missing row channels on the Ag(110) surface. A full monolayer coverage in the simulation was represented by four oxygen molecules in a channel on the slab used to describe the surface in the calculations. One of these adsorbates was assumed to dissociate and yield the "hot" photoproduct. Thus, the coverage in the simulations was determined by the number of adsorbates along a missing row on the substrate. Three effective coverages were examined:  $N_{ad} = 1$ , 2, and 3 adsorbed O<sub>2</sub> (in addition to the dissociating adsorbate). The probabilities for desorption,  $P_{des}$ , as a function of initial energy of the photogenerated oxygen atom, are shown in Figure 24.



Figure 24. CID probabilities vs initial oxygen atom kinetic energy, at the three indicated molecular oxygen coverages; see text for details.

Examination of these results shows that for low  $E_{\rm in}$  values, up to 1 eV, the ratio  $\Gamma = P_{\rm des}(N_{\rm ad} = 3)/P_{\rm des}(N_{\rm ad} = 1)$  is very large, in the range 12–16. This ratio decreases markedly, to  $\Gamma$ = 3, as  $E_{\rm in}$  increases to 3 eV. The initial translational energy of O\* in the O\*/O<sub>2</sub>/Ag(110) system was estimated to be approximately 1 eV.<sup>27</sup> The variation of surface coverage from 0.25 to 1 ML led in the experiment to a 60-fold increase in the CID probability.<sup>23,24</sup> The calculated value of  $\Gamma$  at  $E_{\rm in} = 1$  eV is smaller but demonstrates a similar trend.

Next we examine the variation of polar angle distribution,  $P_{\theta}$ , of desorbates as a function of  $E_{in}$  and the coverage. Figure 25S (see the Supporting Information) exhibits  $P_{\theta}$  for small (0.5 eV) and large (3 eV) incidence energies and for low ( $N_{ad} = 1$ ) and high ( $N_{ad} = 3$ ) coverages. These results clearly indicate that the distributions corresponding to low coverage are broader than those obtained for high coverage. Moreover, for  $N_{ad} = 1$ , the angular distributions show a broad peak near  $\theta = 60^{\circ}$ , whereas for  $N_{ad} = 3$ , the peak of  $P_{\theta}$  is shifted to smaller angles, in the neighborhood of 30°. Except for the yield of desorbates, the angular distributions do not exhibit any marked dependence on the incidence energy. Similar behavior was observed for all other initial energies of the projectile.

The variation of desorption yield and shape of the angular distributions can be explained if the microscopic details of the CID event will be understood. A large number of trajectories, corresponding to various initial conditions, were carefully analyzed. This analysis suggests that the observed features in both  $P_{des}$  and  $P_{\theta}$  can be rationalized by the operation of a cage like behavior in the high coverage cases.

The one-dimensional cage effect is illustrated schematically in Figure 26. Following the dissociation process, the hot O atom moves along the  $\langle 110 \rangle$  direction. Its motion is quasi-onedimensional because of the high potential corrugation along the  $\langle 100 \rangle$  direction. When the O atom approaches an adsorbate, energy is transferred from the projectile to the adsorbed O<sub>2</sub> molecule. The atomic oxygen-substrate equilibrium distance is much shorter than that of the molecular adsorbate. Hence, it is expected that the momentum transfer during the collision will result in the motion of the O<sub>2</sub> along both the  $\langle 110 \rangle$  direction and away from the surface. This is shown in the top panel of Figure 26 by doted arrows. If the target O<sub>2</sub> does not encounter



**Figure 26.** Schematic illustration of the one-dimensional cage effect. The top panel shows the initial arrangement of projectile and neighboring adsorbates. The middle panel illustrates the desorbate trajectory blocking by a neighboring adsorbate. The double lined arrows represent the direction of forces acting on the desorbing molecule. The bottom panel shows the final situation. In all illustrations, dashed line arrows represent the schematic direction of motion of the particle.

another adsorbate and its energy along the surface normal becomes larger than its binding to the substrate, it can leave to the gas phase. In such a situation, the desorbate is expected to leave the substrate with a broad polar angle distribution that is peaked at large angles (far from the surface normal). The distribution is determined by the ratio between the two velocity components of the desorbate, along the  $\langle 110 \rangle$  and surface normal directions. Because the energy transferred by the projectile induces motion predominantly along the surface, the width of the angular distribution will depend on the efficiency of energy transfer to motion along the surface normal. In the low coverage case, this energy transfer between different modes of the desorbate is due to the corrugation it experiences along the  $\langle 110 \rangle$ and  $\langle 100 \rangle$  directions. However, at high coverage, the target O<sub>2</sub> will most probably encounter a neighbor adsorbate during its motion along the substrate. This situation is illustrated in the middle panel of Figure 26. The double lined arrows represent the forces acting on the target O2 because of its collision with the projectile followed by a collision with a coadsorbed molecule. The net force and its final direction of motion is represented schematically by the doted arrow. The bottom panel of Figure 26 illustrates the final result, namely, the desorption angle shifted toward the surface normal. Thus, high coverage can be viewed as a cage for the target molecule that leads to a polar angle distribution that is peaked closer to the surface normal. This can also explain the marked increase in  $P_{des}$  when coverage increases, see Figure 24. The existence of a neighboring adsorbate in the way of the desorbing molecule acts effectively as additional corrugation that increases the energy transfer among the various desorbate modes. Hence, energy transfer from modes parallel to the surface to the normal one are expected to be more efficient resulting in an increase of  $P_{\rm des}$ . Moreover, for large enough energies of the photogenerated

oxygen atoms, the probability to eject more than one adsorbate rapidly increases. The net result is a marked increase of the probability for desorption when coverage ( $N_{ad}$ ) increases from 1 to 3, Figure 24.

#### 6. Conclusions

A number of different collision induced processes were discussed in this review. The first process considered was the CID. Our model system was N<sub>2</sub> CID from the Ru(001) surface. The experimental data suggested that, in the limit of low coverage, the CID cross section increases as a function of projectile incidence energy and seems to converge at high collision energies to a saturation value. In addition, the CID process was found to exhibit a threshold energy below which no desorption is detected. The magnitude of the threshold energy was found to be about twice the binding energy of nitrogen to Ru(001). The experimental results also indicated that the threshold energy is independent of the incidence angle of the collider, suggesting that normal energy scaling is not applicable in this case. At a given  $E_{in}$ , the CID cross section was found to increase by a factor of 4 as the angle of incidence increase from zero (normal incidence) to 60°.

A detailed understanding of the CID results was obtained using molecular dynamics simulations with very good agreement between the experimental and theoretical data. The quality of the agreement suggested that the PES used to describe the system is reliable. The MD calculations indicated that the desorption mechanism involves energy transfer among desorbate modes due to potential corrugation and coupling between translational and frustrated rotational motions. A similar desorption mechanism was found to operate also at high coverage. In the case of high coverage, larger desorption yields were calculated compared to lower coverages. At grazing collisions,  $\theta_{in} = 60^{\circ}$ , we obtained desorption yields larger than unity suggesting that some of the projectiles lead to desorption of more than a single adsorbate.

CID of water from Ru(001) was demonstrated with new insight into the unique isotopically dependent structure of  $H_2O$  and  $D_2O$  on the metallic surface. Selective CID was shown for the more weakly bound molecules within the first bilayer, the  $A_2$  molecules. At thicker ice layers, extremely efficient dissipation of the energetic collider kinetic energy is observed for layers of three bilayers and above, in agreement with recent model MD simulations.

The MD simulations have demonstrated the occurrence of a new CIP, namely, the collision induced migration (CIM) process. It was found that at low coverages CIM could result in surprisingly long migration distances of the target adsorbates. This migration distance decreases markedly when surface coverage is increased to a monolayer. It is argued that the CIM process can play an important role in various surface reactions where the mixing between two (or more) reactants is required.

The CID of O<sub>2</sub> from a Ag(110) surface following the photodissociation of a neighboring oxygen molecule was examined. The experimental study of this system showed strong coverage dependence of the desorption cross section. In addition, a bimodal angular distribution with a forward peak (along the surface normal) and a peak near  $\theta = 45^{\circ}$  was obtained. This data was attributed to the coexistence of two desorption mechanisms: hole induced desorption together with CID where the atomic oxygen formed in the photodissociation process serves as the energetic collider.<sup>23,24</sup> Molecular dynamics simulations confirmed the possibility of CID and demonstrated that the cross section for such an event is indeed very sensitive to

surface coverage. Moreover, the existence of an off normal peak in the angular distribution of desorbates was also shown to result from a CID process. Detailed analysis of the MD results suggests a quasi-one-dimensional cage effect that is responsible to the observed results.

The last process examined was tracer surface diffusion under high gas pressures. Again, the study employed MD simulations to investigate the relation between the magnitude of the surface diffusion coefficient and the gas pressure. The main finding is that in general  $D_{dif}$  increases when gas pressure was changed from zero up to a few hundred atmospheres. This change is manifested by an effective decrease of the activation energy for diffusion as well as a nonuniform change in the preexponential factor. We found that the variation in gas temperature and the nature of the gas-adsorbate interaction does not lead to appreciable change in  $D_{\text{dif}}$ . However, the diffusion coefficient was found to vary markedly when the gas-substrate binding energy is changed. The MD calculations indicated that  $E_{ac}$  at P = 200 atm can decrease by a factor of 4 compared with its value at P = 0 atm provided the gas-substrate binding is large enough. The increase in the gas-substrate binding lead also to the formation of an adsorbed layer that acts to reduce the magnitude of  $D_{\rm dif}$ .

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Supporting Information Available: Full description and illustrations (i.e., Figures 3S, 4S, 5S, 6S, 7S, 9S, 10S, 11S, 13S, 16S, 18S, 20S, 21S, 23S, and 25S) of the material enclosed is available free of charge via the Internet at http://pubs.acs.org.

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