The scattering of gas phase molecules and van der Waals clusters from surfaces

John Norman Beauregard
University of New Hampshire, Durham

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The scattering of gas phase molecules and van der Waals clusters from surfaces

Abstract
The interaction of gas phase species with surfaces plays an important role in a myriad of processes such as heterogeneous catalysis, corrosion and the etching of semiconductor surfaces in the microelectronics industry. Thus, the study of gas-surface interactions has become a field of intense research. In this dissertation, we present the results of a computational study of the scattering of gas phase molecules and van der Waals clusters from surfaces. We have used molecular dynamics calculations which allow for the examination of the microscopic details of gas-surface scattering.

In this work we study four distinct systems. In Chapter I the focus is on the scattering of van der Waals clusters of N$_2$ from crystal surfaces. We find that the cluster-surface scattering dynamics are very different from those observed in monomer-surface scattering. Furthermore, our results are in qualitative agreement with a recent experimental study of the scattering of nitrogen clusters from metal surfaces.

The focus of Chapter II is on the effect of reagent rotation and rotational alignment on the dissociative chemisorption of H$_2$ on metal surfaces. We find that the probability of dissociative chemisorption depends strongly on both the rotational energy and the plane of rotation of the reactant H$_2$. Our results suggest that such information might be useful in uncovering intricate details of the potential energy surface governing these reactions.

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Finally, in Chapter IV we examine the effect of dissolving an H$_2$ molecule in an argon microcluster on the dissociative chemisorption of H$_2$ on a silicon surface. We find that this does, in fact, facilitate the reaction. We also find that the probability of reaction is greater when the H$_2$ occupies a site on the "outside" of the cluster as opposed to "inside".

Keywords
Chemistry, Physical, Physics, Molecular
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The scattering of gas phase molecules and van der Waals clusters from surfaces

Beauregard, John Norman, Ph.D.
University of New Hampshire, 1993
THE SCATTERING OF GAS PHASE MOLECULES AND VAN DER WAALS CLUSTERS FROM SURFACES

BY

John N. Beauregard
B.A. Assumption College, 1986

DISSERTATION

Submitted to the University of New Hampshire in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemistry

September, 1993
This dissertation has been examined and approved.

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Olof E. Echt
Associate Professor of Physics

December 17, 1992
Date
DEDICATION

This work is dedicated to my family, especially my parents Norman H. and Lucienne M. Beauregard. Their love and support are gifts that have enriched my life beyond measure.

I also wish to make special mention of my uncle, Timothy J. Beauregard, who passed away during the preparation of this manuscript. He was a beloved friend and role model to me. Tim will be greatly missed by all who knew him.
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ABSTRACT

THE SCATTERING OF GAS PHASE MOLECULES AND VAN DER WAALS CLUSTERS FROM SURFACES

by

John N. Beauregard
University of New Hampshire, September, 1993

The interaction of gas phase species with surfaces plays an important role in a myriad of processes such as heterogeneous catalysis, corrosion and the etching of semiconductor surfaces in the microelectronics industry. Thus, the study of gas-surface interactions has become a field of intense research. In this dissertation, we present the results of a computational study of the scattering of gas phase molecules and van der Waals clusters from surfaces. We have used molecular dynamics calculations which allow for the examination of the microscopic details of gas-surface scattering.

In this work we study four distinct systems. In Chapter I the focus is on the scattering of van der Waals clusters of N₂ from crystal surfaces. We find that the cluster-surface scattering dynamics are very different from those observed in monomer-surface scattering. Furthermore, our results are in qualitative agreement with a recent experimental study of the scattering of nitrogen clusters from metal surfaces.

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CHAPTER I

THE SCATTERING OF van der WAALS CLUSTERS FROM CRYSTAL SURFACES

Introduction

The scattering of atoms and molecules from crystal surfaces has recently been the object of intensive study [1,2]. The goal of this work is to shed light on the interaction of molecules with surfaces. In atomic scattering, the angular distribution of the scattered species is the primary source of information on this interaction. For molecules scattered directly from a surface, it has been found that the final rotational state distribution of the scattered molecules gives information on the anisotropy of the molecule-surface potential [1-6]. For example, rainbows in the product distribution can, under favorable conditions, be "inverted" directly to yield the potential energy function [6]. In addition, results of both experimental [7-9] and theoretical [10-14] studies indicate that the polarization of scattered molecules is a diagnostic of the molecule-surface potential. In particular, the product rotational alignment ratio (see Appendix A) of an initially rotationally cold incident beam scattered from a crystal surface provides information as to the corrugation of the molecule-surface interaction potential. Rainbows in the rotational projection quantum number (i.e. $m_j$) have been proposed [11(c),13]. Furthermore, in a recent theoretical study, Gerber and coworkers [15] suggested that such alignment ratios could be used to probe isolated adsorbates on a solid surface. Thus, a considerable number of
techniques for investigating the properties of the gas-surface interface now exist, all becoming available since the advent of ultrahigh vacuum techniques and molecular beam technology, as well as modern computers.

Molecular beam techniques have also made it possible to create van der Waals (vdW) clusters of a variety of compositions and sizes [16-20]. This has created a great deal of interest in the structure, stability and dynamics of these clusters. However, the scattering of vdW clusters from solid surfaces has so far received relatively little attention. Those experimental [21-29] and theoretical [30-34] studies that have been carried out show that vdW cluster-surface scattering exhibits dynamics very different from those of monomer-surface scattering. This is not surprising since the dynamics observed result not only from monomer-surface interactions but also from monomer-monomer interactions within the cluster.

The most important concept which has emerged to explain the scattering of clusters from surfaces is the "binary collision model" [30-36]. In this model, the cluster-surface scattering dynamics is viewed as a series of collisions between atoms approaching the surface and those already scattered back from the surface. Thus, an understanding of the binary collision mechanism is central to an understanding of the cluster dynamics as a whole.

Previous theoretical studies by Tully and coworkers [30,31] and recent work by Cleveland and Landman [34] have concentrated on clusters of atoms. However, since one of the most comprehensive experimental studies reports on the scattering of a cluster of N$_2$ molecules [28], it is appropriate that theoretical studies of the scattering of molecular clusters from surfaces be undertaken. Our group is the first to conduct theoretical studies on these more complicated systems [32,33].
In this chapter we try to lay some theoretical foundations for understanding molecular cluster-surface scattering dynamics. In the first section of the chapter we report the results of a classical trajectory study of the scattering of vDW dimers consisting of an N₂ molecule bound to a rare gas (Rg) atom. In the next section we report findings on the scattering of small nitrogen clusters, (N₂)ₙ with n = 2-8.

The fact that the vDW clusters here contain one or more diatoms adds a degree of freedom to the scattering dynamics not considered in previous calculations. With our considerably simplified models we hope to be able to shed some light on the relationship between the cluster dissociation mechanism and the internal degrees of freedom in the scattered monomers. The scattered angular intensity and final rotational state distributions as well as the alignment ratio of diatoms from the scattered vDW clusters are studied in order to gain insight into cluster-surface collision dynamics. In addition, the relationship between the scattering dynamics and cluster geometry is explored.

**The Scattering of N₂-Rare Gas Dimers from Crystal Surfaces**

**Calculations**

Classical trajectory calculations were carried out to simulate the scattering of a model N₂-Rg van der Waals molecule from a rigid surface. We employed the purely repulsive pairwise additive molecule-surface potential of the form used by Proctor et al [10]:

\[ V_{M-S} = \sum_{i=1}^{3} A_i \exp(-\alpha_i z_i) \left[ 1 + \beta Q(x_i, y_i) \right]. \]  

where (xᵢ, yᵢ, zᵢ) are the Cartesian coordinates of atom i. The surface lies in the (x, y) plane and the z-axis is the surface normal. In this equation \( \beta \) is a corrugation parameter and \( Q(x_i,y_i) \) a corrugation term given by:
\[ Q(x, y) = \cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{b}\right), \]  

where \( a \) and \( b \) are surface unit cell lengths in the \( x \) and \( y \) directions respectively. Calculations were performed using two different sets of molecule-surface potential parameters. These are listed in Table 1 as Potential A and Potential B. Potential A is an unspecific noncorrugated surface while the parameters for Potential B are roughly appropriate for the interaction of \( N_2 \) with a silver surface [13].

The intramolecular potential had the form, \( V(\mathbf{r}, \mathbf{R}) = V_{vdW}(R, \gamma) \), where \( \mathbf{r} \) is the interatomic displacement of the diatom, \( \mathbf{R} \) is the displacement of the atom from the \( N_2 \) center of mass, and \( \gamma \) is the angle between \( \mathbf{r} \) and \( \mathbf{R} \). The van der Waals potential had the form of a Morse potential multiplied by a model anisotropy term:

\[ V_{vdW}(R, \gamma) = D \left[ \exp\{2\delta (R_e - R)\} - 2 \exp\{\delta (R_e - R)\} \right] f(\gamma), \]  

where the anisotropy term \( f(\gamma) \) was given by,

\[ f(\gamma) = \{1 + \epsilon \cos^2(\gamma - \gamma_0)\}. \]  

The well depth \( D \) of the \( vdW \) bond was 0.05 eV, while \( \delta \) was 2.0 Å\(^{-1}\) and \( R_e \) was 3 Å. The equilibrium angle \( \gamma_0 \) was taken as either 0° or 90° giving preferred geometries with \( C_{\infty v} \) and \( C_{2v} \) symmetries respectively. The anisotropy parameter \( \epsilon \) was 0.5.

The N-N interaction was taken to be a harmonic oscillator with an equilibrium distance, \( r_e \), of 1.09 Å and a force constant of 10 eV Å\(^{-2}\). The force constant was chosen as to give a relatively stiff N-N bond. This assured the primary internal excitation of the scattered \( N_2 \) diatoms was due to the collisional transfer of translation energy (\( E_{\text{trans}} \)) to rotational energy (\( E_{\text{rot}} \)). This is a reasonable model since it has been shown that, in molecule-surface collisions,
the coupling between $E_{\text{trans}}$ and $E_{\text{rot}}$ is much more efficient than that between translational energy and vibrational energy [37].

The trajectory results presented here are for dimers of either $C_{\infty v}$ or $C_{2v}$ geometry incident along the surface normal. For the present work, the Rg atom had the mass of a nitrogen molecule. The trajectories were initiated with the dimers in their equilibrium geometry and with no internal energy. Data shown are typically Monte Carlo averaged over initial dimer orientation angles and lattice point using 1200 or 1500 trajectories.

**The Binary Collision Model in N$_2$-Rg Dimer-Surface Collisions**

**Results** - Figure I.1 shows the dissociation probability of N$_2$-Rg vdW molecules with $C_{2v}$ symmetry scattered from a surface (Potential A) as a function of collision energy ($E_{\text{coll}}$). The dissociation threshold for N$_2$-Rg vdW dimers occurs at an $E_{\text{coll}}$ of approximately 0.1eV while the dissociation probability plateaus at a maximum of around 50 percent by a collision energy of around 1 eV. Hence, although the threshold for dissociation is close to the vdW bond energy (0.05 eV), the N$_2$-Rg vdW dimers are found to be surprisingly robust as approximately 50 percent remain intact at an $E_{\text{coll}}$ 60 times greater than the vdW bond energy. This was found to be true for dimers of either geometry.

In Figure I.2 we show the dependence of dissociation on the vdW molecule ($C_{2v}$ symmetry)-surface collision geometry at three different collision energies. Here $\zeta_0$ is defined as the initial angle between the vdW bond and the surface normal ($\cos \zeta = \mathbf{R} \cdot \mathbf{z}$). Therefore, $\zeta_0 = 0^\circ$ or $180^\circ$ corresponds to a "perpendicular collision geometry" where the vdW bond is nearly perpendicular to the surface on collision, while $\zeta_0 = 90^\circ$ corresponds to a "parallel collision geometry". Since each trajectory is initiated with the vdW molecule randomly oriented in space (with $\zeta_0$ between $0^\circ$ and $180^\circ$), the trajectories are evenly
distributed on the interval \([-1 \leq \cos \zeta_0 \leq 1]\). In Figure I.2 we show \(\cos \zeta_0\) distribution generated for 1500 trajectories.

For a collision energy of 0.16 eV 28 percent of the vdW molecules dissociate. These trajectories are represented by the shaded region in Figure I.2(a). It is apparent that, in this case, dissociation occurs for collisions where the vdW bond is nearly perpendicular to the surface: The range of dissociative \(\zeta_0\) values falls between approximately 0°-46° and 113°-180°. However, at this \(E_{\text{coll}}\) not all of the trajectories with \(\zeta_0\) values in this range dissociate. As the collision energy is raised to 3.2 eV the fraction of dimers which dissociate increases to 51 percent. Figure I.2(b) shows that at this collision energy dissociation still occurs only for nearly perpendicular collision geometries, while dimers with near parallel collision geometries remain intact. At this higher energy, however, the range of \(\zeta_0\) values leading to dissociation expands to approximately 0°-60° and 120°-180°. Also, at this energy, all of the trajectories with \(\zeta_0\) within the 0°-46° and 113°-180° range dissociate.

We next consider the distribution of the scattered species with scattering angle. In Figure I.3(a) we show schematically the angle of incidence (\(\theta_i\)) and the final scattering angle (\(\theta_f\)) of a molecule scattered from a surface. The angle of incidence is defined as the angle between the path of the incoming molecule and the surface normal. On the other hand, \(\theta_f\) is defined as the angle between the surface normal and the path of the scattered molecule. Figure I.3(b) depicts three different scattering outcomes; (i) subspecular scattering (\(\theta_f < \theta_i\)), (ii) specular scattering (\(\theta_f = \theta_i\)) and (iii) superspecular scattering (\(\theta_f > \theta_i\)). Since all of the trajectory results presented in this section are for \(N_2-\text{Rg}\) vdW dimers incident along the surface normal (\(\theta_i = 0°\)), only specular and superspecular scattering are possible.
Figure I.4 shows the final scattering angle ($\theta_f$) distribution of N$_2$ molecules for both dissociative and nondissociative vdW dimer-surface collisions at an $E_{\text{coll}}$ of 0.8 eV using Potential B. The scattered intensity of both dissociative and nondissociative trajectories peaks at a $\theta_f$ value of around 15°. However, the distribution of the scattered intensity is very different in the two cases. In the case of nondissociated dimers most of the intensity is close to the specular angle of 0°, and has dropped to zero intensity by a $\theta_f$ of 30° (specular scattering is also found to be strongly preferred in monomer-surface scattering). On the other hand, dissociative trajectories show a high degree of superspecular scattering.

**Discussion** - The results presented in Figures I.1, I.2 and I.4 are consistent with observations reported by Xu et al. [29] in a trajectory study of the scattering of small argon clusters from a Pt(111) surface. In that work the high probability of cluster survival was explained by a "binary collision" mechanism for cluster dissociation where the monomer closer to the surface recoils from the surface and undergoes a subsequent collision with the second monomer which is still impinging upon the surface. In order for the monomer-monomer collision to be sufficiently energetic as to cause dissociation, the vdW bond must have a significant component perpendicular to the surface.

The high degree of nonspecular scattering in dissociative trajectories displayed in Figure I.4 is a direct result of the impulsive collision between monomers in the binary collision mechanism. The predominantly specular scattering of nondissociative trajectories suggests that, in these collisions, the monomers avoid each other after recoiling from the surface and, therefore, scatter much like lone molecules. This explains the dependence of dissociation on collision geometry shown in Figure I.2. For a perpendicular collision geometry, the momentum of the first monomer after it recoils from the surface is
in the opposite direction of the momentum of the second monomer. This results in an impulsive collision between monomers.

At low collision energies only trajectories where the vdW bond is very close to perpendicular to the surface will dissociate. However, as shown in Figure I.2, an increase in collision energy leads to an increase in the range of $\zeta_0$ values leading to dissociation. Figure I.2(b) shows that by an $E_{\text{coll}}$ of 3.2 eV, where the dissociation fraction is 51 percent, this range grows to include $\zeta_0 = 0^\circ-60^\circ$ and $120^\circ-180^\circ$. However, the dissociation probability has already reached a maximum of approximately 50 percent by a collision energy of around 1 eV (see Figure I.1). Half of all trajectories will have $\zeta_0$ in this range, leading to a dissociation maximum of around 50 percent. This implies that for collision energies greater than 1 eV the fate of a scattered $N_2$-Rg dimer depends on whether $\zeta_0$ falls between $0^\circ-60^\circ$ and $120^\circ-180^\circ$ (dissociation) or $60^\circ-120^\circ$ (remains intact).

Scattering Dynamics and the van der Waals Dimer Geometry

**Results** - In this work the detailed scattering dynamics of dimers of both the $C_{\infty v}$ and $C_{2v}$ geometry were compared. In Figure I.5 we present, for each cluster geometry, the distributions of (a) the intensity and (b) the average final rotational quantum number, $\langle j' \rangle$, of $N_2$ from dissociated dimers as a function of scattering angle. From Figure I.5(a) it is evident that there is little difference in the scattering intensity distributions for the two geometries: The angular distribution peaks at about $15^\circ$ off specular in both cases, and there is significant nonzero intensity even at large scattering angles. The bottom panel of Figure I.5(b) shows that the distribution of $j'$ with scattering angle depends greatly on dimer geometry. Scattered diatoms from $C_{\infty v}$ dimers become rotationally hotter with increased scattering angle while those of dissociated $C_{2v}$
dimers become rotationally colder. We will use Figure I.6 to help explain these observations.

Figure I.6 shows the dependence of dissociation, final N₂ scattering angle and final N₂ rotational state on the angle ζ₀. These data were obtained by scattering N₂-Rg vdW dimers from a flat surface (Potential B with β = 0) with an E_{coll} of 0.8 eV. Each point in the figure represents the outcome of a single trajectory initiated with the vdW molecule contained in a plane perpendicular to the surface. Once again dissociation was found to have a strong dependence on the ζ₀, with ζ₀ = 0°-60° and 120°-180° leading to dissociation. The top panels of Figures I.6(a) and (b) show that the dependence of the final scattering angle of N₂ on ζ₀ is almost identical for both the C₂v and C₉₀v geometries. This is consistent with the results of Figure I.5(a). Figures I.6(a) and (b) also show, once again, that nondissociative trajectories scatter specularly while dissociative trajectories have a strong tendency for nonspecular scattering. The bottom panels of Figures I.6 (a) and (b) show the dependence of the final rotational state on ζ₀ for both geometries. The two geometries have starkly contrasting behavior: The C₂v produces high j' at ζ₀ near 90°, whereas the C₉₀v produces high j' at ζ₀ near 0°.

In Figure I.7 we show the dependence of j' for a lone N₂ molecule scattered from a flat surface (Potential B with β = 0) with an E_{coll} of 0.8 eV as a function of the N₂-surface collision geometry. The angle φ₀ is defined as the initial angle between the N-N bond vector and the surface normal. It is clear from this figure that the final rotational state of N₂ is very dependent on the N₂-surface collision geometry: Collision geometries where the N-N bond is nearly perpendicular to the surface tend to result in high j', while those where the bond is nearly parallel to the surface result in low j'.
In Figure 1.8 we present data on the (first) alignment ratios \( (b_2/b_0) \) and final rotational state probability as a function of \( j' \) for both geometries. A detailed discussion of the first alignment ratio is given in Appendix A. We present results for dissociative, nondissociative and summed (nondissociative and dissociative) trajectories. The first alignment ratio yields information on the plane of molecular rotation after collision with the surface. Previous calculations and measurements for monomer-surface scattering have usually yielded a roughly monotone decrease from low \( j \), where "helicopter" \((m_j = j)\) can occur, to high \( j \), where "cartwheeling" \((m_j = 0)\) is the only mechanism for angular momentum transfer [11(c)]. The first alignment ratio has an upper maximum of 5 (which corresponds to pure helicoptering) and a minimum value of -2.5 (pure cartwheeling).

The dimer geometry is also observed to have a considerable influence on the product alignments. The summed results (ALL) for the alignment ratio displayed in Figure 1.8 show that the ratio for both geometries decrease monotonically. However, the \( b_2/b_0 \) value for the \( C_{2v} \) geometry is always higher than that of the \( C_{\infty v} \) geometry and never reaches the "cartwheeling" limit of -2.5. The results for the dissociated systems also reflect the usual trend; a monotone decrease as \( j' \) increases. In this case, though, the linear complex has a much lower \( b_2/b_0 \) at a given \( j' \). Finally, the results in Figure 1.8 for the nondissociated clusters show an interesting result. The alignment ratio for the \( C_{\infty v} \) case initially shows an increase as \( j' \) increases rather than a decrease.

The \( P(j') \) results displayed in Figure 1.8 also show a dependence on the dimer geometry. For the summed results, the \( \infty v \) geometry show a higher probability at low \( j' \) and it also has nonzero probability out to higher final rotational states. The probability distributions of \( j' \) for dissociative trajectories are similar for both geometries. However, \( P(j') \) is nonzero out to higher \( j' \). For
nondissociative trajectories the linear geometry show a much higher probability for low $j'$.  

**Discussion** - The geometry dependent data introduced above are easily explained by considering the orientation of the diatom with respect to the surface on collision. As shown in Figure I.7, it is the molecule-surface collision which is primarily responsible for transferring angular momentum to the diatom. For a trajectory at a given angle $\zeta_0$, the orientation of the diatom with respect to the atom and with respect to the surface will be very different, depending on the geometry of the dimer (see the picture at the top of Figure I.6). Hence the different dimer geometries lead to contrasting rotational distributions.

This is reflected in Figure I.6. For the $C_{2v}$ complex, the highest rotational states result from vdW dimer-surface geometries in the in nondissociated region. Hence, $j'$ remains high in the intact dimers, which are scattered close to specular. On the other hand, dissociative trajectories have high scattering angles due to near-central binary collisions. It is clear from Figure I.6(a) that these occur for the $C_{2v}$ complex when the diatom figure axis is parallel to the surface, a geometry which is not suited to high rotational excitation. On the other hand, these same near-central binary collisions occur in the $C_{\infty v}$ complex when the diatom figure axis is nearly perpendicular to the surface, a highly favorable orientation for rotational excitation.

It seems that although the observed angular distribution of each geometry shown in Figure I.5(a) primarily reflects the outcome of the impulsive monomer-monomer collision in the dissociation mechanism of vdW dimers, there is no information on the dimer geometry contained in these data. However, Figure I.5(b) shows that the distribution of the final rotational state of $N_2$ with $\theta_f$ is strongly dependent on dimer geometry. The reason for the contrasting behavior becomes clear when one analyzes the results displayed in
Figure I.7 and considers the geometry of the N$_2$ with the respect to the surface in dissociative and nondissociative collisions for both the C$_{2v}$ and C$_{\infty v}$ geometries. This same argument explains the P(j) data of Figure I.8: The dissociative region for a C$_{2v}$ complex produces low N$_2$ rotation, whereas the opposite is true for the C$_{\infty v}$ case. This is, once again, a reflection of the $\zeta_0$ dependence of the product attributes shown in Figure I.6.

We showed in Figure I.8, that for nondissociated trajectories, dimers with C$_{2v}$ symmetry show a greater tendency towards "helicopter" than do those of C$_{\infty v}$ symmetry. The reason for this is clear from Figure I.6, where the values of $\zeta_0$ leading to dissociation are shown. For the C$_{\infty v}$ geometry dissociation results from molecules colliding with the surface with their figure axis roughly parallel to the surface normal; a situation favorable to high j' production with a predominantly cartwheeling mechanism. This leads to the cartwheeling limit corresponding to a b$_2$/b$_0$ value of -2.5. In contrast, dissociative C$_{2v}$ complexes will tend to collide with the surface with their figure axes perpendicular to the surface normal leading to low j and a greater tendency towards helicopter motion.

Comparison with the uncorrugated surface data of Figure I.2 explains this finding. Those trajectories which are not dissociated in this geometry must have had $\zeta_0$ near 90°. That is, the molecule's figure axis is roughly parallel to the surface. On a flat surface, this geometry cannot give rise to large angular momentum transfer. However, on a corrugated surface, large $\Delta j$ values are possible, and j will often have a considerable component along the z-axis [13].

**Time Dependence of Alignment in Undissociated N$_2$-R$_0$ Dimers**

**Results and Discussion** - The alignment ratio of the diatoms of nondissociated C$_{2v}$ dimers displayed in Figure I.8 shows a trend towards cartwheeling at high j' but does not reach the limit of -2.5 for b$_2$/b$_0$. Further
examination of the trajectories reveals that the value of the alignment ratio depended on the point at which the trajectory was terminated. If the trajectories were allowed to run for a longer period of time they tended to become unaligned (i.e. $b_2/b_0$ shifted towards 0 for all $j$'s). The reason for this is illustrated in Figure I.9. Here we show the time dependence of several variables for a coplanar trajectory with an initial $\zeta$ value of 70° scattered from a corrugated surface using Potential B. The angle $\chi$ is the angle between the angular momentum vector and the surface normal ($\cos \chi = \hat{j} \cdot \hat{z}$), while $R$ is the vdW bond length. For a dissociative trajectory, $R$ increases monotonically after the binary collision, and $\chi$ remains constant as the monomers recede from each other. Figure I.9 shows the contrasting behavior of a nondissociative trajectory. We see that after impact with the surface $\chi$ changes with time and $R$ oscillates. The change in $\chi$ correlates roughly with the vibration of the vdW bond, with the greatest change occurring at the inner turning point. The continued interaction (i.e. multiple collisions) between the atom and diatom via the vibrating vdW bond allows mixing of the diatomic and vdW molecular angular momenta. If an ensemble of trajectories is detected at a macroscopic distance from the surface, the likely result of such mixing is unaligned diatomic rotation.

**Conclusions on N$_2$-Rg vdW Dimer-Surface Scattering**

It is found that the scattering of N$_2$-Rg vdW molecules from crystal surface leads to some interesting and unique dynamics which are very different from those observed in monomer-surface scattering. In particular, it is found that the vdW dimers are surprisingly robust, with around 50 percent remaining intact even at very high collision energies. Also, it is found that the scattering dynamics, particularly the distribution of $j'$ as a function of the final scattering angle and the final rotational alignment, are diagnostics of the cluster geometry.
Examination of the behavior of all (i.e. both dissociative and nondissociative) scattered N$_2$ molecules would seem to indicate that neither the product j distribution nor the alignment ratio yields much information on dimer geometry. However, if undissociated dimers can be distinguished, then measurements of both the rotational temperature with scattering angle and the alignment ratio of these would seem to comprise an excellent source of information on dimer geometry.

The Scattering of Small Nitrogen Clusters from Crystal Surfaces

Previous Work

Early experimental studies on the scattering of vdW cluster beams from metal surfaces showed dynamics very different from that exhibited by monomers. For example, both helium and nitrogen cluster beams were found to recoil with most of the scattering intensity within the scattering plane [22-27], in contrast to monomers, where much of the intensity appears outside the plane. In fact, it was observed that under certain conditions cluster beams of H$_2$ became more intense after scattering from a surface [25]. This generated interest in the use of such "focused" cluster beams as fuel sources for the contained plasmas of fusion reactors.

In a more recent experimental study of the scattering of large N$_2$ clusters from metal surfaces, Bernasek and coworkers sought to link the scattering dynamics to the internal structure of the cluster [28]. Once again, several interesting features were observed in the scattering dynamics. In particular, the clusters showed a high propensity for nonspecular scattering, with a great deal of intensity nearly tangent to the surface. This is in contrast to the case of monomers where the scattered intensity is primarily specular. Also, the rotational temperature of the scattered clusters was found to decrease with increasing scattering angle; this again is the reverse of the monomer case.
In this section we report the findings of a computational study on the scattering of vDW clusters nitrogen molecules from a crystal surface. We compare our findings to those obtained in previous experimental [22-29] and theoretical [30,31,34] studies on the scattering of vDW clusters from surfaces.

Calculations

The Potential Energy Surface - Once again molecular dynamics calculations were used, this time to simulate the scattering of small nitrogen clusters \([ (N_2)_n \text{ with } n = 2,4 \text{ and } 8 \)] from a rigid crystal surface. The atom-surface potential was the same as that given in equation (1), using the parameters for Potential B in Table 1.

The \(N_2-N_2\) interaction potential had the form:

\[
V_{\text{cluster}} = \sum_{i \neq j} V_{ij},
\]

(5)

where \(V_{ij}\) is the interaction between \(N_2\) molecules \(i\) and \(j\) and \(n\) is the number of molecules in the cluster. The \(N_2-N_2\) potential, \(V_{ij}\), is given by:

\[
V_{ij} = V_M + V_{\text{rep}},
\]

(6)

where \(V_M\) is a Morse function:

\[
V_M = D_M \{ \exp[-2\alpha_M (R_{ij} - R_e)] - 2 \exp[-\alpha_M (R_{ij} - R_e)] \}. 
\]

(7)

The function \(V_{\text{rep}}\) is a pairwise additive repulsive interaction between the \(N\) atoms of \(N_2\) molecule \(i\) with those of \(N_2\) molecule \(j\). If the atoms diatom \(i\) are labelled as atoms 1 and 2 and those in diatom \(j\) are labelled as atoms 3 and 4, \(V_{\text{rep}}\) can be written as:

\[
V_{\text{rep}} = \sum_{k=1}^{2} \sum_{l=3}^{4} A_{\text{rep}} \exp(-\alpha_{\text{rep}} d_{kl}).
\]

(8)

where \(d_{kl}\) is the distance between atoms \(k\) and \(l\). The parameters used for equations (7) and (8) in this study are given in Table 2. They were chosen to roughly fit the more sophisticated \(N_2-N_2\) potential of Ling and Rigby [38].
In Table I.3 we compare the vDW well depths, D, and equilibrium bond lengths, R (the distance between N₂ centers of mass), of several different N₂-N₂ geometries using our potential with those of Ling and Rigby [38] whose potential fits condensed phase data well. It is evident that although the well depths for our potential are shallower than those of Ling and Rigby, the overall trend of deepest well for the "crossed" geometry to shallowest well for the "linear" geometry is reproduced. A better choice for Dₘ in equation (7) would probably bring our potential into even better agreement with that of Ling and Rigby.

**Starting Geometries** - Starting (N₂)ₙ cluster geometries for n = 2, 4 and 8 were generated using Metropolis Monte Carlo sampling (see Appendix B). In the case where n = 4 (tetramers) and n = 8 (octamers) calculations were carried out on clusters with two different types of structure which we shall refer to as "ring" and "tight" geometries. The Metropolis Monte Carlo procedure was not employed to generate a thermalized distribution of starting geometries, but rather to produce structures closely resembling the initial geometries shown in Figure I.10 (with the bond distances and angles slightly randomized).

For both tetramers and octamers, the "ring" cluster geometries were generated by carrying out Metropolis Monte Carlo sampling on a starting cluster configuration where the N₂ diatoms were evenly spaced on a circle, the center of mass of two consecutive N₂ molecules separated by Rₑ (see Figure I.10(a) and (b)). Such sampling resulted in ring-like initial geometries where each N₂ had a coordination number of two.

The "tight" geometry clusters were generated by carrying out the same procedure on more close packed starting geometries. In the case of the tetramers, the starting geometry consisted of four N₂ molecules at the corners of a tetrahedron with sides of length Rₑ (see Figure I.10(a)). The starting octamer
geometry consisted of eight N$_2$ diatoms, one on each corner of a cube with
sides of length $R_e$ (see Figure I.10(b)). Thus, the "tight" geometry clusters had
higher coordination so that their structure was more close packed.

In this section we present trajectory results for N$_2$ monomers, (N$_2$)$_2$
 dimers, (N$_2$)$_4$ tetrmers and (N$_2$)$_8$ octamers. The monomer results represent
the outcome of 200 trajectories. The dimer, tetramer and octamer results each
represent the outcome of 50 trajectories. Therefore, for each of the cluster
cases 50 different starting geometries were generated by Metropolis Monte
Carlo sampling. Each trajectory was initiated with the cluster in one of these
starting geometries. The data shown are Monte Carlo averaged over initial
cluster (or monomer in the case of lone N$_2$) orientation angles and lattice point.
The angle of incidence ($\theta_i$) was 60° and the collision energy of 0.4 eV per
nitrogen molecule unless otherwise stated.

Cluster Fragmentation

Results - Figure I.11 shows the survival probability for nitrogen clusters of
various size ($n = 2, 4$ and $8$) after impact on the surface with a collision energy
of 0.4 eV per diatom. We define the survival probability as the ratio of the
number of clusters which survive the collision with the surface intact to those
which dissociate into fragments of smaller clusters. Since the N$_2$-N$_2$ vdW bond
has an approximate dissociation energy of only 0.007 eV, these clusters contain
ample energy for dissociation. The filled triangle represents the results for the
nitrogen dimer. In the case of the tetramer, (N$_2$)$_4$, and the octamer, (N$_2$)$_8$, the
results for two distinct types of geometries are shown. The open circles
represent the findings for clusters with "ring" geometries while the filled squares
correspond to more close packed or "tight" geometries (see Figure I.10). As
with the N$_2$-Rg dimers, the nitrogen dimers show a significant probability of
surviving the collision with the surface. This is also true for the "ring" tetrmers
and octamers. However, for "tight" tetramers and octamers the survival probability falls to zero.

In Figure I.12 we show how the degree of cluster scattering depends on the perpendicular component of the collision energy. The magnitude of this component of the collision energy, $E_\perp$, is given by:

$$E_\perp = (\cos^2 \theta_i) E_{\text{coll}}.$$  

(9)

The data are for "tight" octamers and each point corresponds to a particular collision energy ($E_{\text{coll}}$) and angle of incidence ($\theta_i$). The value $\langle n' \rangle$ represents the mean size of the fragment to which an N$_2$ molecule will belong after the initial cluster scatters from the surface. Hence, the lower the $\langle n' \rangle$ value, the higher the degree of cluster fragmentation. We see that for the lower $E_\perp$ values ($E_\perp = 0.04$ and 0.1 eV per N$_2$), the amount of fragmentation increases with $E_\perp$. However, for perpendicular components to the collision energy of greater than 0.25 eV per N$_2$, the degree of fragmentation remains essentially constant.

In Figure I.13 we show how the size distribution of scattered fragments changes when 50 "tight" octamers are scattered from a surface with a high $E_\perp$ (0.25 eV per N$_2$) where $\langle n' \rangle = 1.06$, as compared to a low $E_\perp$ (0.04 eV per N$_2$) where $\langle n' \rangle = 1.39$. For the higher $E_\perp$ there is a large number of monomers (378), a small number of dimers (11) and no larger cluster fragments. For the lower $E_\perp$ there is still a large number of monomers (299) but fewer than in the high $E_\perp$ case. It is also evident that more of the larger cluster fragments result at the lower $E_\perp$ (32 dimers, 8 trimers and 5 tetramers).

In Figure I.14 we compare the size distribution of the scattered fragments from 50 "tight" octamers with the distribution from 50 "ring" octamers. In both cases the collision energy was 0.4 eV per N$_2$ and the angle of incidence was 60°. In the case of the "tight" octamer ($\langle n' \rangle = 1.28$), once again a large number of monomers are formed (337). There is also a small number of cluster
fragments (20 dimers, 3 trimers, 1 tetramer and 2 pentamers). For the "ring" octamers (<n> = 3.52) there are much fewer monomers (194) but more dimers (30) and trimers (4). The striking feature in this figure, however, is that a number (14) of "ring" octamers remain intact after scattering from the surface.

Discussion - In the previous section on the scattering of N₂-Rg vdW dimers from a solid surface, we showed that the dissociation of a dimer upon impact with a surface involves the transfer of translational energy into internal energy, resulting in the dissociation of the vdW bond. Furthermore, we have shown that in order for a vdW molecule to dissociate a vdW bond must be nearly perpendicular to the surface upon collision.

This same basic model for dimer dissociation can be extended to explain the trends in the survival probability of larger N₂ clusters displayed in Figure I.11. In the case of (N₂)₂ there is only one vdW bond. Hence, the dimer will survive the collision when this bond is nearly parallel to the surface. The result is a 35 percent survival probability under the scattering conditions used in Figure I.11. However, as the size of a "tightly packed" cluster increases the number of vdW bonds within the cluster also increases (see Figure I.10). This should reduce the probability of cluster survival, as it becomes increasingly likely that all of the vdW bonds will be nearly parallel to the surface. Figure I.11 shows this is true for "tight" nitrogen clusters with n = 4 and 8 which have a survival probability of zero. Similar results have been obtained by Tully and coworkers [30] in a molecular dynamics study of the scattering of small argon clusters (Arₙ with n = 5 to 26).

Hence, the dissociation of the larger close packed clusters proceeds in the following way: The N₂ molecules in the "bottom layers" of the cluster scatter from the surface first. As they recede from the surface, these molecules collide with the "upper layers" of the cluster which are still travelling towards the
surface. Thus, some of the cluster collision energy is transferred to internal energy, leading to fragmentation of the cluster. From this model, it is reasonable to assume that the component of the cluster collision energy perpendicular to the surface is primarily responsible for cluster fragmentation. In fact, several groups [28-34] have proposed cluster fragmentation mechanisms where the cluster momentum tangential to the surface is essentially conserved while momentum perpendicular to the surface is used for fragmentation.

On the other hand, the monomers making up the "ring" clusters are joined such that the coordination of each N₂ molecule is two (see Figure I.10). Consequently, when these clusters collide with the plane of the ring nearly parallel to the surface, the vDW bonds are also nearly parallel to the surface. Thus, according to the binary collision model the cluster survival probability should be nonzero. Figure I.11 confirms this by showing that, in fact, around 30 percent of the "ring" tetramers and octamers survive. We believe this to be the first study in which the scattering of "ring-like" clusters from surfaces has been examined.

It has been shown by several groups, both experimentally [24,28] and computationally [31,32], that the degree of cluster fragmentation is dependent on the component of the cluster collision energy perpendicular to the surface. In Figures I.12 and I.13 we show how the degree of cluster fragmentation is dependent upon the perpendicular component of the collision energy, E⊥. In Figure I.12, it is evident that when the E⊥ is relatively small (0.04 or 0.1 eV per N₂), the degree of fragmentation of "tight" octamers increases with E⊥. This means that, in this energy range, that as the impact of the cluster with the surface becomes more energetic, increased internal excitation of the cluster leads to a greater degree of cluster fragmentation.
However, for $E_\perp$ values 0.25 eV or greater the degree of fragmentation remains essentially the same. This is similar to the result obtained for the dissociation probability of $N_2$-Rg dimers as a function of collision energy (Figure I.1). In that case it was shown that a maximum dissociation probability for a vdW dimer with a binding energy of 0.05 eV was reached by $E_{\text{coll}} = 0.8$ eV and remained constant out to very high collision energies. The binding energy of the "tight" $N_2$ octamers, in the geometry depicted in Figure I.10, is approximately 0.1 eV. Hence, it would seem that when the perpendicular component of the collision energy is close to the cluster binding energy, the degree of cluster fragmentation is dependent upon $E_\perp$. On the other hand, when $E_\perp$ is much greater than the binding energy the degree of fragmentation does not vary with increased perpendicular collision energy.

In Figure I.13 we show the size distribution of the scattered fragments from "tight" octamers at $E_\perp$ values in each of the two regions mentioned above; high $E_\perp$ (0.25 eV per $N_2$) and low $E_\perp$ (0.04 eV per $N_2$). In both cases most of the scattered $N_2$ exists as monomers. However, as expected from the data in Figure I.12, when $E_\perp$ is 0.04 eV there are fewer monomers and more cluster fragments (dimers, trimers and tetramers).

The predominance of monomer fragments observed here in nitrogen cluster-surface scattering is in agreement with recent experimental [28] and theoretical [30,31] studies on the scattering of argon clusters from surfaces. However, in an experimental study of the scattering of argon clusters ($Ar_n$ with $n \approx 800$) from a graphite surface, Châtelet et al [29], using cluster collision energies just large enough to cause total cluster fragmentation (similar to our examples with low $E_\perp$), detected a large number of scattered cluster fragments. These findings are in accord with the model for cluster fragmentation described above, and with our results on the dependence of cluster fragmentation with $E_\perp$.
shown in Figures I.12 and I.13. We are currently carrying out a study [39] on the 
scattering of small Arₙ clusters (n = 13, 19 and greater) with scattering 
conditions similar to those used in the experiment of Châtelet et al in the hopes 
of better understanding their findings.

The effect of cluster structure on fragmentation is addressed in Figure 
I.14 which compares the fragmentation of "tight" and "ring" octamers. The "tight" 
octamers (<n' > = 1.28) are found to fragment to a far less extent than the "ring" 
octamers (<n' > =3.52). The major reason for this is seen in Figure I.14 where it 
is shown that 14 out of 50 octamers survive intact. Previously, in explaining the 
30 percent survival probability show by "ring" octamers shown in Figure I.11, we 
stated that when these clusters collide with the plane of the ring nearly parallel 
to the surface, the ring clusters will survive the collision intact.

We have used these findings to explain the existence of possible "magic 
numbers" in the size cluster fragments resulting from the scattering of Ar₁₃ 
clusters from a crystal surface [38]. In this recent work we found that, although 
the predominance of the scattered intensity from the scattering of Ar₁₃ is in the 
form of monomers, the resulting cluster fragments contain unexpectedly large 
numbers of Ar₃ and Ar₅ as compared to other cluster fragments. We attribute 
this to the existence of a number of Ar₃ and Ar₅ rings as subunits in the 
icosahedral structure of Ar₁₃. When the Ar₁₃ cluster strikes the surface with one 
or more of these "subunit" rings parallel to the surface they will survive intact 
much like the N₂ "ring" clusters.

The Angular Distribution of Scattered Intensity

Results - In Figure I.15 we plot the scattered intensity as a function of final 
scattering angle (θ₁) for N₂ monomers, dimers, "tight" tetramers and "tight" 
octamers. The initial scattering angle (θ₁) was 60°. The data presented in this 
figure are summed over all scattered N₂ molecules falling within a given
angular range; monomers as well as those belonging to cluster fragments and intact clusters. In each case (monomer, dimer, "tight" tetramer and "tight" octamer) the peak intensity is near specular. However, as we go from the monomer case to the "tight" octamer case, the amount of specular and subspecular scattering decreases while the amount of superspecular scattering increases.

In Figure I.16 we once again show a plot of the scattered intensity as a function of final scattering angle, this time comparing the results for "ring" and "tight" octamers scattered with a $\theta_l$ of 60°. In both the "tight" and the "ring" cases we find that the intensity peaks near the specular angle ($\theta_l = 60^\circ$). However, as the "tight" octamers show a great deal of superspecular scattering, the "ring" octamers scatter primarily near the specular, with a scattered intensity distribution similar to that displayed in monomer-surface scattering.

In Figure I.17 we show the scattered intensity (normalized to peak) as a function of final scattering angle ($\theta_l$) for N$_2$ molecules from "tight" octamers scattered with $E_{\text{coll}} = 0.4$ eV per N$_2$ and three different angles of incidence ($\theta_i = 0^\circ$, 30° and 60°). When $\theta_i$ is 0°, the only possibilities are for specular ($\theta_i = 0^\circ$) and superspecular scattering ($\theta_i > 0^\circ$). In Figure I.17 we see that this case results in a high degree of superspecular scattering, with the scattered intensity fairly evenly distributed from a $\theta_l$ of 0° out to the maximum of 90°. For a $\theta_i$ of 30°, the scattered intensity distribution is somewhat similar to that for $\theta_i = 0^\circ$. Once again most of the scattering is superspecular ($\theta_l > 30^\circ$), with a maximum at a $\theta_l$ of 45° and extending to final scattering angles nearly tangent to the surface. In this case, however, there is significant subspecular scattering ($\theta_l < 30^\circ$) with some scattering nearly perpendicular to the surface. The profile shown by the scattered intensity for $\theta_i = 60^\circ$ is quite different than in the cases where $\theta_i = 0^\circ$ and 30°. In this instance, the intensity shows a lobular
distribution, showing little subspecular scattering ($\theta_l < 60^\circ$), a peak very close to specular ($\theta_l = 60^\circ$) and a great deal of super specular scattering ($\theta_l > 60^\circ$) out to final scattering angles nearly tangent to the surface.

**Discussion** - As stated above, the scattering of vdW cluster-surface scattering exhibits dynamics very different from those observed in monomer-surface scattering. Perhaps nowhere is this more evident than in the angular distribution of scattered fragments. In early experiments on cluster-surface scattering, for example, both hydrogen and nitrogen cluster beams were found to recoil with most of the scattering intensity within the scattering plane [22,25,26], in contrast to monomers, where much of the intensity appears outside the plane. In fact, it was observed that under certain conditions cluster beams of $\text{H}_2$ became more intense after scattering from a surface [25]. This generated interest in the use of such "focused" cluster beams as fuel sources for the contained plasmas of fusion reactors. More recently, several groups have studied angular distribution of scattered fragments to infer details of the cluster-surface collision dynamics [28-32].

In this section we discuss how the angular distribution of scattered fragments from cluster-surface collisions can be used to gain insight into the mechanism for cluster fragmentation. In Figure 1.15 we see that for "tight" clusters, at a given angle of incidence and collision energy per $\text{N}_2$, the angular distribution distribution of of scattered fragments changes with the size of the initial cluster. Although the peak in each case is near specular, it is evident that the degree of superspecular scattering goes up with cluster size, while the amount of subspecular scattering goes down. Similar findings were obtained by Tully and coworkers in their molecular dynamics study of the scattering of small argons clusters from a metal surface [31].
These findings can be explained by the binary collision model for fragmentation introduced above. In the case of the larger "tight" clusters, when the first layer of monomers scatter from the surface they are prevented from scattering at angles near the surface normal by the upper layers of the cluster. Therefore, these \( \text{N}_2 \) monomers, which undergo multiple monomer-monomer and monomer-surface collisions, will have a tendency to scatter near the surface normal. Hence, the high degree of superspecular scatter in the case of the "tight" octamer. As the initial size of the cluster decreases, it will become less likely that any monomers will become "compressed" by the upper layers of the cluster until, in the extreme case of monomer-surface scattering, the scattering is almost exclusively specular.

The difference in the angular distribution of the scattered intensity displayed between "tight" and "ring" octamers in Figure I.16 can be explained along similar lines. In that figure, "ring" octamers are shown to scatter with a high degree of specular scattering and less superspecular scattering; more like monomers than "tight" octamers. This again is explained by the binary collision mechanism for cluster dissociation.

It was seen in the previous section that the "ring" octamers fragment to a much smaller degree than the "tight" octamers. This implies that during the cluster-surface collision there are fewer multiple, or binary, monomer-monomer and monomer-surface collisions, since it is the number and impulsiveness of these collisions that determine the degree of fragmentation. Hence, fragments from "ring" octamers will show less superspecular scattering than do those from "tight" octamers.

It has also been shown that the scattered intensity distribution is very sensitive to the angle of incidence and, hence, \( E_{\perp} \). In a study of the scattering of large nitrogen clusters from metal surfaces, Bernasek and coworkers [28] found
as the angle of incidence was increased the degree of scattering near the surface normal decreased, while the peak intensity shifted out to final scattering angles nearly tangent to the surface. The results in Figure I.17 are in good qualitative agreement with these findings.

**Final Rotational State of N₂ as a Function of θ₁**

**Results** - In Figure I.18 we display the mean final rotational state, \( \langle j' \rangle \), for scattered N₂ molecules as a function of final scattering angle. We compare the results for scattered monomers, dimers and "tight" octamers. In each case the collision energy was 0.4 eV per N₂ and the angle of incidence was 60°. The scattered N₂ molecules may exist as monomers or belong to cluster fragments. In the monomer case the mean \( j' \) goes up with scattering angle. For the nitrogen dimer, \( \langle j' \rangle \) first increases with \( θ_1 \) in a manner very similar to the monomer case and then decreases to a very low value at final scattering angles near the surface tangent. The results for "tight" octamers also show an initial increase in \( \langle j' \rangle \), although not as dramatic, followed by an overall decrease with \( θ_1 \).

In Figure I.19 we once again plot the mean final rotational state of scattered N₂ molecules as a function of final scattering angle this time as a function of the angle of incidence (\( θ_1 = 0°, 30° \) and \( 60° \)). The results are for "tight" octamers scattered with a collision energy of 0.4 eV per N₂. The results for \( θ_1 = 60° \) are the same as those shown for the "tight" octamer in the previous figure. The \( \langle j' \rangle \) data in this case begins at a final scattering angle of around 45°. However, in the cases where \( θ_1 = 0° \) and \( 30° \) we show data for much lower scattering angles. This is not surprising if one considers the scattered intensity distributions for each of these cases displayed in Figure I.17. In each case displayed in this figure the mean \( j' \) show an initial increase with final scattering angle followed by a monotonic decrease out to scattering angle nearly tangent
to the surface. Also, in each case, as the angle of incidence decreases the degree of rotational excitation increases.

Discussion - We first address the results in Figure I.18. The increase in $<j'>$ with final scattering angle observed for the case of N$_2$ monomer-surface scattering is easily explained. In collisions where the N$_2$ molecule becomes rotationally excited some of the monomers collision energy is converted into rotational energy. In a manner similar to the cluster-surface collision mechanism, this energy comes from the perpendicular component of the collision energy leaving while the momentum tangential to the surface is essentially conserved. Hence, as a rotationally excited monomer scatters from the surface, it will exit at a final scattering angle greater than $\theta_i$: The greater the rotational excitation, the greater the $\theta_i$. For a rigid flat surface

$$\theta_i = \left( \tan^{-1} \left[ \frac{E_{1y}^0}{E_1^0 - E_R} \right] \right)^{\frac{1}{2}},$$

(10)

where $E_{1y}^0$ is the component of the N$_2$ translational energy parallel to the surface, $E_1^0$ is the initial perpendicular component of the translational energy and $E_R$ is the rotational energy due to the N$_2$-surface collision.

In the case of N$_2$ dimers the results shown in figure I.18 can be explained in the following way: It was shown in Figure I.4 for the scattering of N$_2$-Rg vdW dimers, that the N$_2$ molecules of intact dimers scattered predominantly near the specular angle, while those from dissociative collisions showed a high degree of superspecular scattering. This is due to the fact that N$_2$ molecules in dissociative trajectories undergo an impulsive binary collision with the rare gas atom, while those in nondissociative trajectories do not, scattering much like monomers.
Therefore, we can attribute the initial rise in the value of \(<j'>\) with scattering angle seen for nitrogen dimers to \(N_2\) molecules nondissociated dimers, which have been shown to behave like scattered monomers. The subsequent decrease in the mean \(j'\) after a \(\theta_1\) of 65° is due to fragment monomers. The most probable cause of the lower average \(j'\) in these cases is deactivation of \(N_2\) molecules which are initially rotationally "hot" after the initial cluster-surface collision by the subsequent monomer-monomer collision. This same argument can be extended to explain the results shown for the "tight" octamer. These results are in qualitative agreement with the experimental findings of Bernasek and coworkers [28] in a study of the scattering of large \(N_2\) clusters consisting of approximately 5000 molecules from metal surfaces. In that work it was found that the rotational temperature of the scattered fragments decreased as a function of the final scattering angle.

The results in Figure I.19 for the scattering of "tight" octamers at three different angles of incidence, show the same general trend as displayed in Figure I.18. However, in this figure it is apparent that the degree of rotational excitation increases as the angle of incidence decreases. This can be attributed to the fact that, as the angle of incidence decreases \(E_{\perp}\) increases. Hence, from our model for cluster fragmentation the larger \(E_{\perp}\) should result in increased internal excitation of the cluster upon impact with the surface. This result is also in agreement with the findings of Bernasek and coworkers [28].

Conclusions on \(N_2\) Cluster-Surface Scattering

We have shown that several phenomena evidenced in nitrogen cluster-surface scattering can be explained by the concept of binary collisions. For example, it is found that the the survival probability of a cluster after it collides with the surface decreases dramatically as the number of internal binary collisions increases, while the degree of cluster fragmentation increases. The
stability of a cluster in such impacts is, therefore, highly sensitive to the geometry of the cluster; in particular to the number and proximity of nearest neighbors.

We also find that the results for our molecular dynamics simulation of the scattering of small nitrogen clusters from surfaces agrees qualitatively with the experimental results reported by Bernasek and coworkers [28] for much larger clusters. In particular we find, as they did, that as the angle of incidence increases there is less scattering normal to the surface, while the peak intensity shifts to final scattering angles nearly tangential to the surface. We also find, as in the experiment, that the amount of rotational energy in the scattered N$_2$ decreases with final scattering angle. This is in direct contrast to monomer-surface scattering where the rotational energy of scattered monomers is found to increase with $\theta_f$. These results are explained by the binary collision mechanism for cluster dissociation.
REFERENCES


Figure I.1  Probability of dissociation of N₂-Rg vdW dimers as a function of collision energy ($E_{coll}$). The N₂-Rg dimers have $C_{2v}$ symmetry and the atom surface potential is Potential A.
Figure I.2  Dependence of $\text{N}_2\text{-Rg}$ dimer dissociation on $\zeta_0$ (see text). The probability distribution of $\cos\zeta_0$ for 1500 trajectories is displayed. The shaded area corresponds to dissociated trajectories. The $\text{N}_2\text{-Rg}$ dimers have $C_{2v}$ symmetry and the atom surface potential is Potential B.
Figure I.3  Pictorial definition of several terms used in molecule-surface scattering. (a) Pictorial representation of the angle of incidence ($\theta_i$) and the final scattering angle ($\theta_f$) of a molecule scattered from a surface. (b) Pictorial representation of the (i) subspecular, (ii) specular and (iii) superspecular scattering of a molecule from a surface.
Figure I.3

(a) Surface Normal

Incident Molecule

Angle of Incidence $\theta_i$

Final Scattering Angle $\theta_f$

Scattered Molecule

Surface

(b) Surface Normal

(i) Subspecular Scattering $\theta_f < \theta_i$

(ii) Specular Scattering $\theta_f = \theta_i$

(iii) Superspecular Scattering $\theta_f > \theta_i$

Surface
Figure I.4  Scattered intensity (normalized to peak) as a function of scattering angle ($\theta_i$) for dissociated and undissociated N$_2$-Rg dimers with $C_{2v}$ symmetry. The angle of incidence ($\theta_i$) is 0° and $E_{\text{coll}} = 0.8$ eV. The atom-surface potential is Potential B.
Figure I.5  Intensity and mean final rotational state as a function of scattering angle ($\theta_l$).  (a) Intensity (normalized to peak) as a function of $\theta_l$ for dissociated dimers of both geometries.  Initial conditions and atom-surface potential are the same as in Figure I.4.  (b) Mean final rotational quantum number for N$_2$ monomers resulting from dissociation as a function of $\theta_l$.
Figure I.6  Action-angle plot for N2-Rg dimers with both geometries. (a) Final rotational quantum number and (b) scattering angle as a function of $\zeta_0$ (see text) for both geometries scattered from a flat surface (Potential B with $\beta = 0$) with $E_{\text{coll}} = 0.8$ eV. The trajectories were initiated with the vdW dimer contained in a plane perpendicular to the surface. Dissociative and nondissociative regions are indicated.
Figure I.7  The dependence of the final rotational state of N$_2$ monomers scattered from a surface (Potential B) on the N$_2$-surface collision geometry. The angle $\phi_0$ is defined as the angle between the N-N bond vector and the surface normal.
Figure I.8 First alignment ratio \((b_2/b_0)\) and final rotational distribution as a function of \(j\) for both geometries. Dissociative, nondissociative and summed results are shown.
Figure I.9. Time-dependent plot of a typical nondissociative trajectory of preferred C$_{2v}$ geometry scattered from a surface using (Potential B). The angle $\chi$ is the angle between the j vector and the surface normal. $R$ is the vDW bond length, and $z_{c.m.}$ is the height of the diatom center of mass above the surface.
Figure I.9

\[ \begin{align*}
\chi & [\text{deg.}] \\
R & [\text{a.u.}] \\
Z_{\text{c.m.}} & [\text{a.u.}]
\end{align*} \]

Time [ps]
Figure I.10  Typical initial cluster geometries used for the Metropolis Monte Carlo sampling: (a) "Ring" tetramers and octamers and (b) "Tight" tetramers and octamers.
Figure I.11  The survival probability of ($N_2)_n$ clusters ($n = 2, 4$ and $8$) as a function of cluster size. The filled triangle represents the results for dimers. For the tetramers and octamers the results for both "ring" (open circles) and "tight" (filled triangle) starting geometries are shown. The data are for cluster collision energies of 0.4 eV per $N_2$ and an angle of incidence of $60^\circ$. 


Figure I.12  The degree of cluster fragmentation as a function of the perpendicular component of the collision energy ($E_\perp$) per N$_2$ ($E_\perp = E_{\text{coll}}\cos^2\theta_i$). The data are for "tight" octamers. Each point corresponds to a particular collision energy, $E_{\text{coll}}$, and angle of incidence, $\theta_i$. The value $<n>$ represents the mean size of the cluster fragment to which an N$_2$ molecule will belong after the initial cluster scatters from the surface.
Figure I.13  Comparison of the size distribution of scattered fragments from the scattering of 50 "light" octamers for two different perpendicular energy components, $E_\perp = 0.25$ eV per $N_2$ (filled squares) and $E_\perp = 0.04$ eV per $N_2$ (open circles).
Figure I.13

![Graph showing the number of fragments vs. fragment size for different energy levels.]

- $E_\perp = 0.25$ eV per N$_2$
- $E_\perp = 0.04$ eV per N$_2$
Figure I.14  Comparison of the size distribution of the scattered fragments from both "tight" octamers and "ring" octamers. In each case, the data shown are the result of 50 trajectories initiated with a collision energy of 0.4 eV per $N_2$ and an angle of incidence of 60°.
Figure I.14

- "Tight" Octamer
- "Ring" Octamer

Number of Fragments

Fragment Size

52
Figure I.15 Scattered intensity (normalized to peak) as a function of final scattering angle ($\theta_f$) for the $N_2$ molecules of from scattered monomers, dimers, "tight" tetrarbers and "tight" octamers. The initial scattering angle ($\theta_i$) is $60^\circ$. The intensity includes all scattered $N_2$ molecules (i.e. scattered monomers as well as those belonging to cluster fragments and intact clusters).
Figure I.16  Scattered intensity (normalized to peak) as a function of final scattering angle ($\theta_i$) for both "ring" octamers and "tight" octamers. The initial scattering angle ($\theta_i$) is 60°. The intensity is summed over all scattered N$_2$ molecules (i.e. scattered monomers as well as those belonging to cluster fragments and intact clusters).
Figure I.17  Scattered intensity (normalized to peak) as a function of final scattering angle ($\theta_f$) for N$_2$ molecules from "tight" octamers scattered with $E_{\text{coll}} = 0.4$ eV per N$_2$ and three different angles of incidence ($\theta_i = 0^\circ$, 30$^\circ$ and 60$^\circ$).
Figure I.18  Mean final rotational state, $\langle j' \rangle$, for scattered N$_2$ molecules as a function of final scattering angle. The results shown are for scattered monomers, dimers and "tight" octamers. In each case $E_{\text{coll}} = 0.4$ eV per N$_2$ and $\theta_i = 60^\circ$. The scattered N$_2$ molecules include monomers and those belonging to cluster fragments.
Figure I.19  Mean final rotational state, $\langle j \rangle$, for scattered N$_2$ molecules as a function of final scattering angle. The results shown are for "tight" octamers with $E_{\text{coll}} = 0.4$ eV at three different angle of incidence ($\theta_i = 0^\circ$, 30° and 60°). The scattered N$_2$ molecules include monomers and those belonging to cluster fragments.
Table I.1  Molecule-surface potential parameters.

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<th>Parameter</th>
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<th>Potential B</th>
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<td>A</td>
<td>20 eV</td>
<td>20 eV</td>
</tr>
<tr>
<td>α</td>
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<td>2 Å⁻¹</td>
</tr>
<tr>
<td>β</td>
<td>---</td>
<td>0.12</td>
</tr>
<tr>
<td>a</td>
<td>----</td>
<td>2.89 Å</td>
</tr>
<tr>
<td>b</td>
<td>----</td>
<td>2.89 Å</td>
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Table I.2. \( \text{N}_2\text{-N}_2 \) potential parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>( D_M )</td>
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</tr>
<tr>
<td>( \alpha_M )</td>
<td>2 Å(^{-1})</td>
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<tr>
<td>Equation (8)</td>
<td></td>
</tr>
<tr>
<td>( R_e )</td>
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</tr>
<tr>
<td>( A_{rep} )</td>
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</tr>
<tr>
<td>( \alpha_{rep} )</td>
<td>2.17 Å(^{-1})</td>
</tr>
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</table>
Table I.3  A comparison of vdW well depths (D) and equilibrium bond

distances (R) for the N₂-N₂ interaction potential used in this work

and that used by Ling and Rigby [37]. Examples are shown for

several dimer geometries.

<table>
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<th>Geometry</th>
<th>This Work</th>
<th>Ling and Rigby [37]</th>
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<td>&quot;Crossed&quot;</td>
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<td>R = 3.60 Å, D = -1.282 x 10^{-2} eV</td>
</tr>
<tr>
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<td>R = 3.6 Å, D = -1.2 x 10^{-2} eV</td>
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<tr>
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<tr>
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<td>R = 4.0 Å, D = -3.63 x 10^{-3} eV</td>
<td>R = 4.7 Å, D = -1.98 x 10^{-3} eV</td>
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CHAPTER II

THE ROLE OF REAGENT ROTATION AND ROTATIONAL ALIGNMENT IN THE DISSOCIATIVE CHEMISORPTION OF HYDROGEN ON METAL SURFACES

Introduction

The study of dissociative chemisorption of gas phase molecules on metal surfaces is important to the understanding of a myriad of processes such as heterogeneous catalysis, electrode reactions and corrosion, to name but a few [1,2]. Recent advances in molecular beam, laser and surface detection technologies have made it possible to study the reactions of monoenergetic molecular beams with clean, well characterized metal surfaces [3-17]. Similarly, the development of modern fast computers has made it possible to carry out theoretical studies which complement this experimental work [17-34]. A central goal of these experimental and theoretical studies is to probe the details of the potential energy surface (PES) which governs the chemisorption process.

The dissociative chemisorption of H$_2$ on metals:

$$H_2(g) + S \rightarrow 2H-S$$  \hspace{1cm} (1)

(where S represents the surface) is among most studied classes of gas-surface reactions [6,11,14-17,19-20,23-25,27(a),28(c),29-30,32-34]. The H$_2$-metal systems provide prototypical examples of the dissociative chemisorption process, and it is hoped that the knowledge obtained from the study of these
relatively simple processes will lead to a better understanding of more
gas-surface reactions. In this chapter we present the results of a quasiclassical
trajectory study on the dissociative chemisorption of H₂ on several different
model metal surfaces. In particular, we examine the role of the rotation and
rotational alignment (see Appendix A) in the reagent H₂ molecule on the
reactivity of these systems.

In what follows, we first survey the research done on the effect of reagent
translational (T), vibrational (V) and rotational (R) energy on dissociative
chemisorption. We focus on the analogies between this area of research and
the corresponding gas phase work. We next describe briefly the calculations
performed in our study of the dissociative chemisorption of H₂ on metal
surfaces. Finally, we present and discuss our findings on the effect of reagent
rotation on such reactions.

**Dissociative Chemisorption Studies: Analogies to the Gas Phase**

**The Roles of Translation and Vibration**

A common approach to investigating the dynamics of reactive processes
has been to examine the effects of reagent translational (T), vibrational (V) and
rotational (R) energy on the probability of reaction. Such studies have proven
very fruitful in the study of elementary gas phase reactions [35-51]. In fact, the
effects of T and V on gas phase reactions have been subjects of great interest
for quite some time [35-42], and the role each of these modes of excitation plays
in gas phase reactions of the type A + BC → AB + C (where A, B and C
represent atoms) is fairly well understood. In general, it is found that an
increase in either T or V results in a monotonic rise in the reaction probability.
Furthermore, the well known Polanyi rules [35-36] provide generalized
guidelines for the relative effectiveness of T and V in such reactions. For
example, it would be expected that V would be more effective in promoting
reaction with a late activation barrier; that is a barrier to reaction that occurs after the bond under attack has begun to stretch. Conversely, T is expected to be more efficient in reactions with early barriers.

Similarly, a great deal of work has been carried out on the effect of the translational energy of the reactant molecule on dissociative chemisorption at metal surfaces [3-13,15-17]. These studies have also been used to obtain valuable information on the nature of the PES governing the reaction. For example, such studies often reveal whether or not dissociative chemisorption is activated, and if so, the magnitude of the barrier to reaction. More recently, the relative efficacies of T and V in promoting dissociative chemisorption have been examined [7,8,11,13,15,16]. In particular, it has been found that V can be as effective as T in overcoming the barrier to reaction in the activated dissociative chemisorption of H₂ on Cu(111) [11,16(a)]. These findings are in agreement with theoretical studies [33(a)] which employ a PES where the barrier to reaction occurs after the H-H bond begins to stretch. Borrowing from the field of gas phase reaction dynamics, as discussed above, these results are taken as evidence of a late barrier to reaction in the dissociative chemisorption of H₂ on Cu(111).

The Role of Rotation

Considering the great success enjoyed in relating the effects of T and V on reactivity in simple gas phase and gas-surface reactions to certain features in the reaction PES, it is logical to ask whether any useful information might be obtained by studying the effect of rotation (R). In fact, several gas phase studies [41-47] (most theoretical in nature) have predicted a much richer structure in the reaction probability as a function of R, in contrast to the monotonic rise in the reactivity observed with increasing T or V. It has been suggested [43,46,49-51] that this more complicated rotational dependence might be unfolded to yield
even more intricate details of the reaction PES than those revealed by T and V dependence data.

Unfortunately, compared to translation and vibration, the role of reagent rotation in gas phase reactions has received comparatively little attention. A major reason for this is that, until recently, it was believed that R would have little effect on reactivity in these systems. However, recent experimental [41] and theoretical [42, 44-48] studies have given evidence to the contrary. In fact, a general trend has emerged in the reaction cross section, \( \sigma \), as a function of the diatomic rotational quantum number, \( j \), for a large class of gas phase reactions which proceed through a linear transition state: At low \( j \) \( \sigma(j) \) decreases, passes through a minimum and then increases with higher \( j \). This effect is more prominent at low collision energies. At high collision energies \( \sigma(j) \) often simply increases monotonically with \( j \). Also, it has been shown theoretically [48] that rotational excitation leads to profound hydrogenic isotope effects in gas phase reactions of the type:

\[
A + HB(j) \rightarrow AH + B \text{ or } AB + H; \tag{2}
\]

and is often more efficient than either T or V in promoting hydrogen atom abstraction [48(b)].

In addition, trajectory studies have shown the effect of R in gas phase reactions to be a diagnostic of the potential energy surface [43,49-51]. For example, in a classical trajectory study, Mayne and Minick [49] gave evidence that rotation promotes reaction more readily on potential energy surfaces with late barriers to reaction. Also, Harrison and Mayne [50] have shown that unusual oscillatory behavior in \( \sigma(j) \) can be used to uncover spurious “bumps” in model potentials.

As in the gas phase, the role of R in dissociative chemisorption on metal surfaces has received little attention when compared to T and V. The principal
reason for this is that experiments which directly measure the effect of R on these reaction are not yet feasible. The only experimental results which address the role of rotation in dissociative chemisorption come from rotational state measurements in recombinative desorption studies [52-53]. It is possible for individual atoms chemisorbed on a surface to travel, or diffuse, about the surface. Recombinative desorption, the reverse process of dissociative chemisorption, occurs when two such atoms join to form a gas phase molecule. For example the recombinative desorption of H₂ from a surface can be written as:

\[ 2\text{H-S} \rightarrow \text{H}_2(\text{g}) + \text{S}. \]  

(3)

In an experiment [52], Zare and coworkers measured the j distributions of H₂ and D₂ desorbed from the Cu(110) and Cu(111) surfaces. They found that although these distributions had a mean rotational energy somewhat less than \( kT_s \) (where \( k \) is the Boltzmann constant and \( T_s \) is the surface temperature), they did not deviate significantly from a Boltzmann distribution. Since the measured rotational state distributions seemed to have enhance populations at low j, application of the principle of detailed balancing led Zare and coworkers to propose that rotation might slightly hinder dissociative chemisorption.

However, a subsequent recombinative desorption study by Michelson, Rettner and Auerbach [53] has presented results suggesting that the role of R in dissociative chemisorption may, in fact, be quite complex. In this study, the velocity distributions of D₂ molecules desorbed from the Cu(111) surface were measured for a wide range of distinct rovibrational \((v, j)\) states (with \( v = 0, 1 \) and \( 2 \) and \( j = 0 \) to 14). It was found that the mean translational energy of desorbed D₂ displayed nonmonotonic behavior as a function of \( j \): The energy first increased with \( j \), reached a maximum at \( j = 5 \) and then decreased with higher \( j \) values. Application of detailed balancing to these data indicates that R inhibits
the dissociative chemisorption of D₂ on Cu(111) at low j, but enhances reactivity at high j. This trend is remarkably similar to that observed in the study of gas phase reactions (see above).

Also, several theoretical studies have been performed which suggest the possibility of interesting rotational effects in dissociative chemisorption. Calculations on dissociative chemisorption have been performed which suggest that increased rotational energy facilitates the reaction [24(a), 28(a), 29], hinders the reaction [27(b), 34(c)], has little effect on the reactivity [25(a)] or has a considerable but complex and nonsystematic effect on the reactivity [17, 24]. Furthermore, dynamical calculations [28(a), 30] indicate dissociative chemisorption is highly dependent upon the angular momentum quantum number, mₗ, which determines the orientation of the molecule's plane of rotation with respect to the surface.

Calculations

H₂-Metal Potential Energy Surfaces

The reactivity of H₂ on transition metal surfaces is due primarily to the ability of the surface to act as a source of electrons. A very simple, and quite qualitative, description of the dissociative chemisorption process is as follows: As the H₂ molecule approaches the surface, the surface donates electrons from its conduction band to the antibonding orbital of the H₂. This begins to weaken the H-H bond. At the same time the H-surface bonds begin to form. Eventually, the H-H interaction becomes negligible and the two separated atoms become chemisorbed on the surface.

However, such a simple description of the dissociative chemisorption process neglects several important features that may be present in the H₂-metal PES (excellent discussions of the reactive interactions between molecules and metal surfaces are given in references 54 and 55). For example, before the...
minimum corresponding to the dissociative chemisorption product (two chemisorbed H atoms), the potential may contain one or more local minima along the reaction path. At relatively long H₂-surface distances, the molecule may become physisorbed on the surface. Such an interaction (analogous to a van der Waals bond) is only weakly attractive and the molecule remains intact. Still closer to the surface, the molecule itself may become chemisorbed. In molecular chemisorption, the H₂ is usually more strongly bound to the surface than in physisorption and, although the H-H bond is not broken, it is weakened and displays lower frequency vibrations than in the gas phase [54]. Furthermore, successive minima may be separated by potential energy barriers corresponding to energies of activation for going from one minimum to the next.

Also, electronic structure calculations [18,19] show that the nature of the H₂-surface interaction can change dramatically as a function of the orientation of the molecule with respect to the surface. More specifically, it is found that the barrier to dissociative chemisorption is lowest for H₂-surface geometries where the diatom bond axis is parallel to the plane of the surface [18,19]. As the diatom-surface geometry moves towards a configuration where the H₂ bond axis is perpendicular to the plane of the surface, the H-H stretch experiences greater resistance [19] and the barrier to chemisorption increases. Hence, geometries where the bond axis of the H₂ is nearly parallel to the surface are expected to be conducive to dissociative chemisorption. On the other hand, dissociative chemisorption is unlikely for geometries where the H-H bond is nearly perpendicular to the surface.

Modified LEPS potentials of the type introduced by McCreery and Wolken [56(a)] have been quite successful in qualitatively reproducing the important features in the diatom-surface interactions. Also, these potentials provide a great deal of versatility in their ability to represent a variety of model
systems, exhibiting any combination of the features mentioned above, by variation of the potential parameters. We shall illustrate this fact in what follows, as we discuss the modified LEPS potentials we employed to model the interaction of $H_2$ with the Ni(100) and W(001) surfaces.

**The Diatom-Surface Coordinate System** - Shown in Figure II.1 is the coordinate system for the $H_2$-W(001) system. The surface is contained in the $(x,y)$ plane and the $z$ axis is the surface normal. In Figure II.1(a) we show a view looking down the normal at the $(x,y)$ plane. We label three different points on the W(001) lattice; the 1 CN or "atop" site, the 2 CN or "bridge" site and the 5 CN or "fourfold" site. The term CN refers to the coordination of an atom chemisorbed at each respective site. Note that the lattice spacing for the W(001) surface is 3.16 Å. The coordinate system of the Ni(100) surface is similar to that of the W(001) surface except that the lattice spacing is 2.5 Å.

Figure II.1(b) contains the full Cartesian coordinate system with the surface in the $(x,y)$ plane. Here we define the angle $\theta$ as the angle between the $z$ axis and the diatom bond vector. The angle $\theta$ is important in discussing the variation of the $H_2$-surface potentials, and hence reactivity, with the diatom-surface geometry.

**The $H_2$-W(001) Potential** - We employed the LEPS potential of McCreery and Wolken [23, 56] to model the interaction between an $H_2$ molecule and the W(001) surface. This potential is formulated in terms of three two body interactions, one between the two H atoms of the diatom, and one between each H atom and the surface. It is given by:

$$V_{H_2-W} = \frac{1}{1+\Delta}\left[U_1 + U_2 + U_3 - \left(A_1^2 + (A_2 + A_3)^2 - A_1(A_2 + A_3)\right)^{\frac{1}{2}}\right], \quad (4)$$

where
\[ U_i = \frac{D_i}{4} \left\{ (3 + \Delta) \exp[-2\alpha_i(r_i - r_{0i})] + (2 + 6\Delta) \exp[-\alpha_i(r_i - r_{0i})] \right\}, \]  \hspace{1cm} (5)

and

\[ A_i = \frac{D_i}{4} \left\{ (1 + 3\Delta) \exp[-2\alpha_i(r_i - r_{0i})] + (6 + 2\Delta) \exp[-\alpha_i(r_i - r_{0i})] \right\}. \] \hspace{1cm} (6)

This potential reduces to a Morse oscillator representing a lone H\(_2\) molecule in the asymptotic region of the reactant channel and to a sum of two Morse functions (one for each H-W(001) interaction) in the product channel. The parameters \(D_i, \alpha_i\) and \(r_{0i}\) are the dissociation energy, Morse parameter and equilibrium distance of the \(i^{th}\) two body interaction. The atom-atom interaction is labelled by \(i = 1\), whereas, \(i = 2\) and \(3\) correspond to the atom-surface interactions. \(\Delta\) is an adjustable Sato parameter which allows flexibility as to the position and the height of the barrier to reaction. This allows for the modelling of systems with a variety of features (e.g. activated and nonactivated chemisorption, early and late barriers to reaction, physisorption or molecular chemisorption wells etc.).

As displayed in Figure II.1, the W(001) surface is taken to lie in the \((x,y)\) plane, while the \(z\) axis represents the distance above the surface. In order to model the corrugation of the W(001) surface the parameters \(D_i, \alpha_i\) and \(r_{0i}\) for the H atom-surface interactions \((i = 2\) and \(3)\) are modulated as a function of the positions of the atoms above the W(001) lattice. Hence, for \(i = 2\) and \(3\) the values of \(D_i\) and \(r_{0i}\) are given by:

\[ D_i(x_i,y_i) = D_i \left[ 1 + \delta Q(x_i,y_i) \right], \] \hspace{1cm} (7)

and

\[ r_{0i}(x_i,y_i) = z_m \left[ 1 + \epsilon P(x_i,y_i) \right]. \] \hspace{1cm} (8)

The corrugation function \(Q(x_i,y_i)\) has the form:

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\[ Q(x, y) = \cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) - A \left[ \cos\left(\frac{2\pi x}{a}\right) - 1 \right] \left[ \cos\left(\frac{2\pi y}{a}\right) - 1 \right], \]  

(9)

where \( a \) is the lattice parameter for the W(001) surface (3.16 Å). The corrugation function \( P(x_i, y_i) \) was given the form:

\[ P(x, y) = \cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) - B \left[ \cos\left(\frac{2\pi x}{a}\right) - 1 \right] \left[ \cos\left(\frac{2\pi y}{a}\right) - 1 \right]. \]  

(10)

The atom-surface Morse parameters were also taken to be a function of position over the lattice and were given by:

\[ \alpha_i(x_i, y_i) = \left[ \frac{1.488 \text{ eV} \text{ Å}^{-1}}{D_i(x_i, y_i)} \right], \]  

(11)

for \( i = 2 \) and \( 3 \). The values of the parameters used to model the H\(_2\)-W(001) [23,56] system are given in Table II.1. We have performed calculations on the H\(_2\)-W(001) using two different Sato parameters, \( \Delta \), which give two distinct potential energy surfaces.

**H\(_2\)-W(001) [Surface I]** - For the first H\(_2\)-W(001) PES, which we shall refer to as Surface I, we use a Sato parameter of −0.08. Figure II.2 contains a contour plot for this PES (zero on this potential corresponds to two infinitely separated gas phase H atoms). In this figure, the H\(_2\) is held with its bond axis parallel to the surface plane (\( \theta = 90^\circ \)) and along the x axis. The diatomic center of mass is held fixed over the 1 CN site. The coordinate \( Z_{c.m.} \) in this plot corresponds to the distance of the H\(_2\) center of mass above the surface. The H-H bond distance increases as the H atoms are moved in opposite directions along the x axis. As discussed above, this molecule-surface geometry is expected to be conducive to the dissociative chemisorption of H\(_2\).

In the asymptotic region of the reactant channel (the lower right hand corner of the figure), the potential corresponds to a gas phase H\(_2\) molecule.
The binding energy of the H$_2$ molecule relative to 0 is 4.74 eV. On the other hand, in the reactant channel (the top left corner of the plot), the potential corresponds to the sum of two atom-surface interactions. The well corresponding to the two chemisorbed H atoms has a minimum value of -6 eV when the atoms sit atop the two 1 CN sites adjacent to, and on opposite sides of, the central 1CN site (an H-H bond length of approximately 12 a.u. or twice the lattice parameter, a). We shall refer to this as "atop to atop" dissociative chemisorption. The PES displays an activation barrier for this process of 0.55 eV in the entrance channel and a 1.8 eV barrier for the reverse process, recombinative desorption [56(a)]. Furthermore, the barrier to dissociative chemisorption is found to increase as the H$_2$-surface geometry changes from parallel to perpendicular.

This is illustrated in Figure II.3 which contains a contour plot for Surface I in which the H$_2$ bond axis is held perpendicular to the plane of the surface over the 1 CN site (θ = 0°). The plot coordinate Z$_1$ corresponds to the distance of the lower H atoms from the surface. The H-H bond length increases as the upper H atom is moved away from the surface with the lower atom at a fixed Z$_1$ value. It is apparent from this figure that perpendicular geometry will not lead to dissociation since the H-H stretch will experience great resistance. Please note, however, the existence of a well corresponding to the adsorption of intact H$_2$ (in the region of Z$_1$ = 3 a.u. and an H-H bond length of 2 a.u.). This physisorbed state has a minimum energy of -3.9 eV. The barrier to this physisorption state from free H$_2$ is 0.82 eV, while the barrier for the reverse process is 0.02 eV. The physisorbed state is bound by 0.9 eV relative to H(g) + H-W.

H$_2$-W(001) [Surface III] - For the second H$_2$-W(001) potential, which we shall refer to as Surface II, we take Δ to be 0.10. In Figure II.4 we show a
contour plot for Surface II in which the H$_2$ molecule is held parallel to the plane of the surface. This plot is analogous to that displayed in Figure II.2 for Surface I. Note the presence of a well corresponding to what can be characterized as a molecularly chemisorbed H$_2$ (the well is highlighted by tick marks). This well has a binding energy of 0.67 eV with respect to free H$_2$ and there is no activation barrier to this state from free H$_2$. Once again, as in Surface I, the well corresponding to the two chemisorbed H atoms has a minimum value of -6 eV for "atop to atop" dissociation. There is a small activation barrier of 0.06 eV for going from the molecular chemisorption state to the dissociative chemisorption well.

In Figure II.5 we show a contour plot for Surface II in which the H$_2$ is held perpendicular to the plane of the surface. This plot is analogous to that displayed in Figure II.3 for Surface I. Once again it is apparent that, for a perpendicular diatom-surface geometry, the H-H stretch is hindered. However, this plot shows no sign of a physisorption well for H$_2$ for this geometry as in Figure II.3.

**The H$_2$-Ni(100) Potential** - The potential energy surface used to model the H$_2$-Ni(100) surface is that employed by Cruz and Jackson [34(c)] in their mixed quantum-classical study of H$_2$ dissociative chemisorption. The H$_2$-Ni(100) potential is modified slightly from the H$_2$-W(001) potential given above. The potential is given by:

$$V_{H_2-Ni} = U_1 + U_2 + U_3 + \left[ A_1^2 + (A_2 + A_3)^2 + A_1(A_2 + A_3) \right]^2.$$  

(12)

This time there is an individual Sato parameter given for each of the two body interactions, leading to the following expressions for $U_i$ and $A_i$:

$$U_i = \frac{D_i}{4(1 + \Delta_i)} \left\{ (3 + \Delta_i) \exp[-2\alpha_i(\xi - \xi_0)] + (2 + 6\Delta_i) \exp[-\alpha_i(\xi - \xi_0)] \right\}. \quad (13)$$

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and

\[ A_i = \frac{D_i}{4(1 + \Delta_i)} \left\{ (1 + 3\Delta_i) \exp\left[ -2\alpha_i (\eta - r_0) \right] + (6 + 2\Delta_i) \exp\left[ -\alpha_i (\eta - r_0) \right] \right\}. \]  

(14)

In order to account for surface corrugation, the equilibrium bond length and well depth for the atom surface interactions \( i = 2 \) and \( 3 \) are varied with with the position over the lattice. Hence, for \( i = 2 \) and \( 3 \):

\[ r_{0_i} = z_0 [1 + \varepsilon Q(x_i, y_i)], \]  

(15)

and

\[ D_i = D_0 [1 + \delta Q(x_i, y_i)]. \]  

(16)

where the corrugation term \( Q(x_i, y_i) \) is given by

\[ Q(x_i, y_i) = \left[ \cos \frac{2\pi x_i}{c} + \cos \frac{2\pi y_i}{c} \right]. \]  

(17)

The Ni(100) lattice constant, \( c \), has a value of 2.5 \( \text{Å} \). The other parameters for the \( \text{H}_2\)-Ni(100) potential are given in Table II.2.

In Figure II.6 we show a contour plot for the \( \text{H}_2\)-Ni(100) potential in which the diatom is held with its bond parallel to the surface (analogous to Figures II.4 and II.2). Unlike the “atop to atop” dissociative chemisorption preferred in both \( \text{H}_2\)-W(001) cases, Figure II.6 shows that on the Ni(100) surface \( \text{H}_2 \) prefers to dissociatively chemisorb, over an atop site, such that the two H atoms occupy the two 2 CN sites on either side of the 1 CN site. We shall refer to this as “atop to bridge” dissociative chemisorption. The well corresponding to the two chemisorbed H atoms has a minimum value of -4.7 eV, essentially the same energy as the free \( \text{H}_2 \) molecule.

In Figure II.7 we show a contour plot for the \( \text{H}_2\)-Ni(100) potential in which the \( \text{H}_2 \) is held perpendicular to the plane of the surface (analogous to that displayed in Figures II.3 and II.5 for the \( \text{H}_2\)-W(001) potentials). Once again it is apparent that, for this diatom-surface geometry, the H-H stretch is hindered,
Neither contour plot for the H$_2$-Ni(100) potential shows any well corresponding to physisorbed or molecularly chemisorbed H$_2$ such as those found in the H$_2$-W(001) potentials.

**The Dynamics Calculations**

In our calculations the metal surfaces were held rigid. This has been shown to be a reasonable approximation for H$_2$-metal surface systems [25, 28(a,c), 29], due primarily to the difference in mass between the H$_2$ molecule and the metal atoms of the surface. For example, it has been calculated [29(b,c)], within the hard sphere model, that the average energy exchanged between the H$_2$ molecule and a W(001) surface is only 2 percent of the initial H$_2$ collision energy.

Quasiclassical trajectory calculations [42] were used to solve the dynamics of the diatom-rigid surface system. Each trajectory was initiated with the diatom randomly positioned above the surface lattice and far enough from the surface so that the diatom-surface interaction was negligible. The initial center of mass velocity of the molecule was normal to the surface. The coordinates and momenta representing the initial quantum state of the diatom (v, i, m$_j$) were chosen using the method of Porter et al [57]. In the case of the nonaligned trajectories, the magnetic quantum number m$_j$ was chosen randomly between -j and j. For the aligned results a single m$_j$ value was used throughout an entire run. At the energy range considered in this study there are only two possible outcomes for a H$_2$-surface collision:

1. Dissociative Chemisorption - where the H-H bond is broken and two atom surface bonds are formed, and
2. No Reaction - where the H$_2$ recoils from the surface intact.

Trajectories were terminated when they could be classified as having one these two outcomes.
The Effect of Reagent Rotation and Rotational Alignment in H2 + Ni(100)

Results and Discussion

The Effect of Collision Energy on Reactivity - In Figure II.8 we show the effect of the center of mass collision energy ($E_{\text{coll}}$) of H2 on the dissociative chemisorption of H2 on Ni(100). These data are for H2 in its ground rovibrational state and incident along the surface normal. We find that the reaction probability is already 0.29 by an $E_{\text{coll}}$ of only 0.01 eV, reflecting the small barrier to dissociative chemisorption of the H2-Ni(100) system. As $E_{\text{coll}}$ is increased from 0.01 eV the reaction probability rises sharply, reaching a value of 0.63 by a collision energy of 0.2 eV. For $E_{\text{coll}}$ greater than 0.2, however, it appears as though the reaction probability is beginning to plateau: As the value of $E_{\text{coll}}$ is doubled from 0.2 eV to 0.4 eV, probability of reaction increases to only 0.73.

Comparison to Mixed Quantum-Classical Studies - In Figure II.9 we compare some of the quasiclassical trajectory (QCT) results for H2 + Ni(100) obtained in this work with the corresponding time dependent mixed quantum-classical (MQC) results of Cruz and Jackson [34(c)] (both studies used the same PES). We display the probability of dissociative chemisorption for several rovibrational states (v, j) as a function of $E_{\text{coll}}$. Once again, as seen in Figure II.8, the QCT results show a high probability of reaction at low collision energies. However, it is apparent that in the cases where v is 0 (j = 0, 1 and 2) the QCT results are always higher than the MQC results at low $E_{\text{coll}}$. Nevertheless, for j values of 0 and 1 the QCT and MQC results are in good agreement after an $E_{\text{coll}}$ of 0.1 eV. The results for j = 2 also converge, but not until a collision energy of around 0.25 eV. Also, in each case where v = 0, the reaction probability for both the QCT and MQC results rises with collision energy, converging to a reaction probability of around 0.60 by an $E_{\text{coll}}$ of 0.3 eV.
In the case of the (1, 0) state, the QCT results agree quite well with the MQC results even at low $E_{\text{coll}}$. In this case, when $v = 1$ the reaction probability for both methods plateaus at a value of around 0.8-0.9 at a very low collision energy.

The disparity between the MQC and QCT results for $v = 0$ at low collision energies is not unexpected. Chiang and Jackson [34(b)] obtained similar results in a previous study where time dependent quantum mechanical results were compared with those obtained from quasiclassical trajectories. A $\text{H}_2$-Ni(100) potential of reduced dimensionality (2-D) was used in both cases. Chiang and Jackson concluded that the lower reaction probabilities observed in the low energy quantum results are due, primarily, to the quantum mechanical property of barrier reflection. When a quantum mechanical particle encounters a barrier, it may be reflected even if it has more energy than is required to surmount the barrier. The reflection coefficient, in fact, can be quite large if the energy of the particle is near that of the barrier [34(b)]. Although the PES for the $\text{H}_2$-Ni(100) system has only a very small barrier to dissociative chemisorption, in quantum mechanics a barrier exists corresponding to the zero point energy in the saddle point region. Also, as discussed above, the barrier to dissociative chemisorption becomes substantial for nonparallel $\text{H}_2$-surface geometries. For the $\text{H}_2(1,0)$ case, the energy of the $\text{H}_2$ is relatively high before one even considers $E_{\text{coll}}$, since $v = 1$ corresponds to 0.8 eV of vibrational energy. Therefore, when $\text{H}_2$ is in its first excited vibrational state the results for the MQC and QCT methods converge at low collision energies.

Another factor which may contribute to the disagreement of the MQC with the QCT results at low energies is the fact that the mixed quantum-classical results are for a fixed position above the lattice (the 1 CN site), while the quasiclassical trajectory results randomly sample the entire Ni(100) lattice. It
has been found [28(c), 34(c)] that dissociative chemisorption can be highly dependent on the lattice site, particularly at low energies. At higher energies this site dependence tends to lessen.

The Effect of Rotation - In both cases considered (QCT and MQC) in Figure II.9, the reaction probability is found to decrease as j increases from 0 to 2. This trend led Jackson and Cruz to conclude that rotation acts to hinder dissociative chemisorption. Similar behavior was observed by Lee and DePristo in a QCT study on the dissociative chemisorption of H₂ on Ni surfaces. Both groups have proposed that the decrease in reactivity is a direct result of the strong variation of the H₂-Ni(100) potential with the diatom-surface geometry. As we discussed above, the barrier to dissociative chemisorption is smallest for molecule-surface geometries where the diatom bond axis is parallel to the surface and becomes quite large for perpendicular geometries. Hence, "parallel" H₂-surface collisions are more reactive than "perpendicular" collisions. In fact, through the observation of individual trajectories, we find that for j = 0 the H₂ molecules tend to be "funnelled" into parallel geometries as they approach the surface. A rotating molecule, however, is more likely to rotate out of the favored geometry for reaction. Hence, the decrease in reactivity displayed in Figure II.9 is ascribed to rotational disruption of the "funnelling" effect.

Figure II.10 contains QCT results for the reaction probability for H₂(0,j) + Ni(100) for a series of collision energies and for a larger range of j values than considered in the previous figure. We show data for a series of collision energies, 0.01 eV to 0.4 eV. For lower collision energies (0.01 eV and 0.1 eV, shown in the lower panel), we find that the reaction probability decreases with the first 2 or 3 j states (in agreement with the trend shown in Figure II.9), reaches a minimum, and then increases monotonically at higher values of j. In
the case where $E_{\text{coll}}$ is 0.01 eV the reaction probability increases from 0.29 at $j = 0$ to 0.71 by $j = 8$. Surprisingly, we find that for $j \geq 5$ the reaction probability for a collision energy of 0.01 is greater than that for an $E_{\text{coll}}$ of 0.1 eV.

The top panel of Figure II.10 contains results for two higher collision energies (0.2 eV and 0.4 eV) as well as those for an $E_{\text{coll}}$ of 0.10 eV (for comparison to the lower panel). In the case of these higher collision energies, we once again see the "dip and climb" behavior in the reaction probability as a function of $j$. It is also apparent that for higher collision energies the "dip" in the reaction probability extends out to higher $j$ values. However, at the same time, the initial decrease in the reaction probability curve becomes less pronounced. The behavior displayed in Figure II.10 is comparable to that predicted by Michelsen, Rettner and Auerbach [53] for $D_2 + \text{Cu}(111)$ on the basis of recombinative desorption data. Furthermore, in view of the data presented in Figure II.10, it is apparent that the explanation for the effect of rotation on the dissociative chemisorption of H$_2$ on Ni(100) suggested by Cruz and Jackson is incomplete. An explanation which accounts for the increase in the reaction probability at high $j$ is required.

As mentioned above, the "dip and climb" behavior in reaction probability as a function of $j$ was first observed in the gas phase [46]. A simple model PES has been used by Mayne and coworkers to account for this behavior [47,49,50(b)]. In this model, gas phase reactions of the type AB + C are treated as coplanar systems with zero impact parameter, in which the symmetric stretch is vibrationally adiabatic. The reaction occurs along a reaction coordinate, $s$, proceeding from reactants ($s = -\infty$) to products ($s = \infty$). The only other degree of freedom is the angular rotation of the atom with respect to the diatom center of mass, $\gamma$. Asymptotically, motion in $\gamma$ corresponds to diatom rotation. Near the transition state it corresponds to bending of the A-B-C complex.
In Figure II.11 we show a purely qualitative example of such a reduced potential. The reaction coordinate, s, is plotted along the x axis, while the angular coordinate, γ, is plotted along the y axis. The contour lines increase in potential energy as γ goes from 0° to 90° or -90°. The PES is essentially isotropic in γ at large negative values of s. This corresponds to the freely rotating AB molecule. In the transition state region (s = 0), however, the potential is highly anisotropic in γ. A minimum energy geometry is obtained for γ = 0°. This corresponds to the favored collinear transition state, for which the lowest barrier to reaction is encountered. However, as γ changes towards 90° or -90° (corresponding to nonlinear transition state complexes) the activation barrier increases dramatically. Thus, the anisotropy in the PES creates a "saddle point" region through which a trajectory must travel in order to react.

For j = 0, gas phase reactions of the type AB + C display a "funnelling" effect similar to the one we have observed in dissociative chemisorption. In the gas phase, however, the reactants are funneled into a linear transition state. At energies near threshold, motion in γ tends to deflect the trajectory away from the saddle point on the reduced potential. This is explained by the fact that a trajectory with nonzero j approaches the transition state region at an angle, effectively narrowing the width entrance of the channel to reaction. Thus, the decrease in reactivity at low j in the gas phase is attributed to a rotational "orientation" effect.

However, at higher j the extra energy available from rotation (for the reduced potential the rotational energy goes as j²) allows trajectories to climb higher on the walls in the saddle point region. Thus, the trajectory has access to a wider opening to the transition state region of the PES. This "energetic" effect acts to increase the probability of reaction. Eventually, the "energetic" effect overcomes the "orientation" effect and the reactivity begins to increase.
with j. Finally, at high collision energies, the ability of the potential to deflect trajectories is decreased. Thus, the "orientation" effect is washed out, eventually resulting in a monotonic increase in the reaction probability as a function of j. We believe that the above explanation for the trends for the effect of rotation in gas phase reactions can be modified to explain the similar trends we observe in $H_2(0,j) + Ni(100)$.

Consider the dissociative chemisorption of $H_2$ on Ni(100) with the $H_2$ center of mass fixed above the 1 CN site. The lowest energy route to reaction (the reaction path) occurs for a geometry where the $H_2$ is fixed parallel to the surface ($\theta = 90^\circ$) with the bond along the x axis. Now consider the effect of varying $\theta$. In this simple picture we restrict this motion to the (x,z) plane, a model analogous to a coplanar AB + C reaction in the gas phase. Far from the surface the $H_2$-Ni(100) interaction is essentially isotropic and motion in $\theta$ corresponds to rotation of the free $H_2$ molecule in a plane perpendicular to the surface. However, as we discussed earlier, the $H_2$-Ni(100) PES is highly anisotropic, with the barrier for chemisorption increasing dramatically as the molecule is rotated from a parallel to a perpendicular geometry. Therefore, close to the surface motion in $\theta$ corresponds to restricted rotation of the $H_2$ in the transition state region.

Therefore, a reduced potential energy surface, similar to that shown in Figure II.11 for the gas phase AB + C reaction, can be envisioned for $H_2 + Ni(100)$. In this case, however, the saddle point region is created as one rotates the $H_2$ from its preferred "parallel" geometry ($\theta = 90^\circ$) near the transition state to one where the $H_2$ bond axis is perpendicular to the surface ($\theta = 0^\circ$ or $180^\circ$). As in the gas phase, the "orientation" effect should be predominant for low j (at low $E_{coll}$) causing the reaction probability to decrease. As j increases, the increased energy due to rotation will eventually allow the "energetic" effect to overtake the
"geometry" effect and the reaction probability will begin to rise with \( j \). Finally, at high collision energies, the orientation effect will begin to get washed out and the initial decrease with \( j \) will become less pronounced. Eventually, when \( E_{\text{coll}} \) becomes high enough (although not shown in Figure II.10) the reaction probability should increase monotonically with \( j \).

**The Effect of Rotational Alignment** - We next examine the effect of rotational alignment (see Appendix A) of \( H_2 \) on the dissociative chemisorption of \( H_2 \) on Ni(100). The parameter \( \lambda \) is defined by:

\[
\lambda = \frac{|J_z|}{|J|},
\]

(18)

where \( J \) is the angular momentum vector and \( J_z \) is its z component (recall that the z axis is the surface normal). Hence, a \( \lambda \) value of 0 corresponds to rotation in a plane perpendicular to the surface, while a \( \lambda \) of 1 represents rotation in a plane parallel to the surface. In Figure II.12 we show the reaction probability for \( H_2(0, j) + \text{Ni}(100) \); for \( j = 2, 5 \) and \( 8 \), and a collision velocity of 0.01 eV, as a function of \( \lambda \). The results show that, for all three \( j \) states examined, the probability for reaction is greatest when the plane of diatom rotation is parallel to the surface and lowest when the plane of rotation is perpendicular to the surface. In each case there is a monotonic rise in the reaction probability as \( \lambda \) increases from 0 to 1.

This trend is a direct result of the anisotropy of the \( H_2 \cdot \text{Ni}(100) \) potential (with respect to \( \theta \)) in the transition state region. We explain by discussing the two extremes (\( \lambda = 0 \) and 1). In the case where \( \lambda = 0 \), the \( H_2 \)-surface geometry oscillates between parallel (\( \theta = 90^\circ \)) and perpendicular (\( \theta = 0^\circ \) and \( 180^\circ \)) configurations. This case is very similar to the simplified picture we used to explain the effect of \( j \) on the reaction probability. Recall that in that model the
lowest barrier for dissociative chemisorption was encountered for "parallel" H_2-surface geometries while the greatest barrier was encountered by "perpendicular" geometries. Hence, when the plane of rotation is parallel to the surface, a trajectory samples the full anisotropy of the H_2-Ni(100) potential (as a function of θ) near the transition state. As a result, the "geometric" effect, which is due to this anisotropy and tends to deflect trajectories away from the "saddle point" region, will be strongest when λ = 0.

In the case where λ = 1, the plane of rotation of the H_2 molecule is fixed parallel to the surface. As a consequence of this, the H_2 bond axis is parallel to the surface (θ = 90°). As we discussed earlier, such "parallel" molecule surface geometries encounter the lowest barrier to chemisorption. Also, since θ stays fixed at 90° the trajectory does not sample the anisotropy of the potential near the reaction region, and the "geometric" effect will be minimized. Thus, it should come as no surprise that the greatest reaction probability for rotating H_2 comes for λ = 1. All other values of λ represent intermediates in a transition between these two extremes.

**The Effect of Reagent Rotation and Rotational Alignment in H_2 + W(001)**

**Results and Discussion**

**The Effect of Collision Energy on Reactivity** - In Figure II.13 we show the effect of the H_2 center of mass collision energy (E_{coll}) on the dissociative chemisorption of H_2 on W(001) [Surface I]. These QCT data are for H_2 in its ground rovibrational state and incident along the surface normal. The threshold for dissociative chemisorption is observed at a collision energy of 0.6 eV. As E_{coll} is increased, the reaction probability rises steadily to a value of 0.43 at a collision energy of 1.1 eV.

The threshold for reaction of 0.6 eV for H_2-W(001) [Surface I] indicates that chemisorption is an activated process for this system: Recall the PES,
shown in Figure II.2, displayed a 0.55 eV barrier to chemisorption along the reaction path. It is also evident that, in the range of collision energies examined here, the reaction probability does not reach its maximum value, as it shows no sign of a leveling off or decreasing at high $E_{\text{coll}}$.

In Figure II.14 we show the effect of the $H_2$ center of mass collision energy ($E_{\text{coll}}$) on the dissociative chemisorption of $H_2$ on W(001) [Surface II]. Once again, these data are for $H_2$ in its ground rovibrational state and incident along the surface normal. In this case, the threshold for dissociative chemisorption occurs at 0.06 eV (1 out of 400 trajectories reacted at this $E_{\text{coll}}$).

As the collision energy is increased, the reaction probability rises monotonically to a value of 0.81 at a collision energy of 0.5 eV, where it shows signs of beginning to plateau.

These data indicate that dissociative chemisorption is also activated on Surface II. The activation barrier correlates well to the 0.06 eV barrier to chemisorption found along the Surface II reaction path. However, the threshold is much lower than that observed for Surface I.

**The Effect of Rotation** - Figure II.15 contains QCT results for the reaction probability for $H_2(0,j) + W(001)$ [Surface I] for $j$ values ranging from 0 to 8. We show data for a series of collision energies (0.5 eV to 1.1 eV). The lower panel contains data for the three lowest collision energies (0.5, 0.6 and 0.7 eV). At a collision energy of 0.5 eV, there is no reaction for $j$ values of 0 through 7. However, a threshold for reaction at this $E_{\text{coll}}$ is observed at $j = 8$ (3 out of 600 trajectories reacted). For a collision energy of 0.6 eV, the reaction probability rises monotonically with $E_{\text{coll}}$ from a value of 0.005 at $j = 0$ to a value of 0.08 by $j = 8$. Finally, at a collision velocity of 0.7 eV the reaction probability rises from 0.06 at $j = 0$ to a value of 0.22 by $j = 8$. 

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The results in the lower panel of Figure II.15 eV are very revealing. We observed in Figure II.13 that for H$_2$(0,0) on Surface I, a collision energy of 0.5 eV was just slightly below the threshold for reaction. However, for an E$_{\text{coll}}$ of 0.5 eV there is no reaction until a j value of 8, which corresponds to the addition of 0.80 eV in rotational energy. This indicates that, on this PES, rotation is not effective in overcoming the barrier to dissociative chemisorption (which is "early" in this case). However, once the collision energy is large enough to overcome the activation barrier (>0.55 eV), additional rotational energy is effective in enhancing the reaction.

The top panel of Figure II.15 contains results for four higher collision energies (0.8, 0.9, 1.0 and 1.1 eV). In this panel, we see a very different behavior in the reaction probability as a function of j. The trend in each case is the same: The reaction probability rises, sometimes relatively sharply, as j goes from 0 to 3. It remains relatively unchanged between j = 4 to 6. It then rises slightly for j values of 7 and 8. This behavior is most pronounced for the highest collision energy, 1.1 eV.

The dependence of the reaction probability as a function of j displayed in the upper panel of Figure II.15, for cases with high E$_{\text{coll}}$, is clearly different from any of the lower collision energy cases shown in the bottom panel. This is evidence that, perhaps, a different region of the PES is being sampled at these higher energies. The most striking feature of the results in the top panel of Figure II.15 is the sharp increase in the reaction probability with the first few j values. This feature is most pronounced at a collision energy of 1.1 eV. At this E$_{\text{coll}}$, the reaction probability rises from 0.43 to 0.70 as j increases from 0 to 3 (which corresponds to an increase in rotational energy of only 0.09 eV). However, an additional 0.44 eV of rotational energy, corresponding to an increase from j = 3 to j = 8, increases the reaction probability to only 0.79. This
would seem to indicate that, in this case, the primary role of rotation in facilitating the reaction is not to contribute energy, but to induce some sort of dynamical effect.

Figure II.16 contains QCT results for the reaction probability for $H_2(0,j) + W(001)$ [Surface II] for $j$ values ranging from 0 to 8. We show data for two collision energies, 0.10 and 0.20 eV. Both collision energies show the same trend: The reaction probability increases sharply as $j$ goes from 0 to 1. It then decreases with $j$, reaches a minimum, and increases with larger $j$. Thus, in this case, we observe both the sharp rise with initial $j$ observed for $H_2$-$W(001)$ [Surface I], and also the "dip and climb" behavior observed for the $H_2$-$Ni(100)$ system.

The sharp rise in the reaction probability with initial $j$ values observed for both $H_2$-$W(001)$ surfaces is not explained by the argument we presented to account for the behavior of the reaction probability as a function of $j$ observed in $H_2(0,j) + Ni(100)$. In fact, this new finding runs counter-intuitively to that argument. This points to the existence of a feature in the $H_2$-$W(001)$ potential energy surfaces which does not occur for the $H_2$-$Ni(100)$ system. Examination of the contour plots displayed in Figure II.3 [Surface I] and Figure II.4 [Surface II] show the existence of either a physisorption or molecular chemisorption well for $H_2$ in each PES. No such well is found for the $H_2$-$Ni(100)$ system.

Figure II.3 contains a contour plot for the $H_2$-$W(001)$ system for a geometry where the $H_2$ is perpendicular to the surface. Recall that this plot shows evidence of a physisorption well for molecular $H_2$ and that the barrier to this well from free $H_2$ is 0.82 eV. Also note that it is quite possible that the well may persist for $H_2$-surface geometries slightly away from perpendicular. Since the activation energy for $H_2$ physisorption is so large, only trajectories with high
$E_{\text{coll}}$ will access the well. These are precisely the cases for which we see the
sharp rise in the reaction probability with initial $j$ values.

Figure II.4 shows the existence of what can be classified as a molecular
chemisorption well for $H_2$ at parallel diatom-surface geometries. There is no
activation energy to this well. Correspondingly for Surface II, we observe a
sharp rise in the reaction probability with initial $j$ even at low collision energies
(0.10 and 0.20 eV in Figure II.16). However, as in the top panel of Figure II.15
for Surface I, this effect is more pronounced for the larger collision energy.

If $H_2$ is physisorbed or molecularly chemisorbed on a surface, it is
possible for it to undergo multiple collisions with the surface. Hence, it may
have several opportunities to obtain a diatom-surface geometry favorable for
reaction and, therefore, it has an increased probability of reacting. We propose
that the sharp increase in the reaction probability with initial $j$ observed for both
$H_2$-W(001) potentials is a direct consequence of the existence of the
physisorption and chemisorption wells mentioned above.

Kara and DePristo [28(a)] obtained similar results in a QCT study on the
dissociative chemisorption of $N_2$ on W(110). In a previous study [28(b)], they
had determined that dissociative chemisorption in this system involved a
mechanism where the $N_2$ underwent multiple collisions with the W(110) surface
before it obtained a geometry favorable to reaction. A detailed analysis of
individual trajectories [28(a)], revealed that rotationally excited $N_2$ had
increased residence times on the surface compared to nonrotating $N_2$ with
identical collision energies. The increased residence time allowed for more
$N_2$-surface collisions and, hence, a greater probability of reaction.

We believe that a similar effect occurs for the $H_2$-W(001) potential energy
surfaces used in this study. However, a detailed analysis of the dissociative
chemisorption dynamics of Surface I and Surface II has not yet been carried

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Such a study should prove quite useful in unravelling the dynamics leading to the observed trends in the reaction probability as a function of j.

The Effect of Rotational Alignment - We next examine the effect of rotational alignment (see Appendix A) of H₂ on the dissociative chemisorption of H₂ on W(001) [Surface I]. In Figure II.17 we show the reaction probability for H₂(0, j = 2, 5 and 8) + W(001) [Surface II] at a collision velocity of 0.70 eV, as a function of λ. For j = 2 and 8, the results show the same trend as observed for the H₂ + Ni(100) system: The probability for reaction is greatest when the plane of diatom rotation is parallel to the surface and lowest when the plane of rotation is perpendicular to the surface. In both cases there is a monotonic rise in the reaction probability as λ increases from 0 to 1. However, for j = 5 a somewhat startling result is obtained. At this j value, the reaction probability rises, as expected, as λ goes from 0 to 0.8. However, at λ = 1 a totally unexpected drop in the reaction probability occurs. Since this data point seemed suspiciously close to that obtained for j = 2 (λ = 1), it was recalculated using both a different number trajectories and different random numbers to generate initial conditions. The results were the same. At this time we are at a loss to explain this totally unexpected behavior in the reaction probability as a function of the rotational alignment of H₂.

Conclusions

Our quasiclassical trajectory calculations for the dissociative chemisorption of H₂(0,j) on three model metal surfaces show several interesting features in the reaction probability as a function of j. We have attributed the observed trend in reactivity to specific features in the potential energy surfaces governing the reactions. However, these assertions are tentative and a more detailed analysis is required before any solid conclusion are reached.
We also find that the probability of dissociative chemisorption has a strong dependence on the rotational alignment of the reactant H₂ molecules. In general, this dependence is consistent with our explanations for the effect of j on the reactivity.
REFERENCES


Figure II.1  The H2-W(001) coordinate system. (a) View looking down the z-axis. The points 1 CN, 2 CN and 5 CN represent 3 different sites for chemisorbed H atom. (b) View from the side: The surface lies in the (x,y)-plane and the z-axis is the surface normal. The angle $\theta$ is the angle between the diatom bond vector and the surface normal.
Figure II.2  Contour plot for the H$_2$-W(001) potential (Surface I) with a parallel molecule-surface geometry (i.e. H$_2$ molecule is parallel to the plane of the surface with its center of mass over the 1 CN site). $Z_{c.m.}$ is the distance of the H$_2$ center of mass from the surface. The contour lines are spaced by 0.5 eV. The $-2$ eV contour line is labelled at the top of the graph for reference.
Figure II.3  Contour plot for the $\text{H}_2$-$\text{W}(001)$ potential (Surface I) with a perpendicular molecule-surface geometry (i.e. $\text{H}_2$ molecule is perpendicular to the plane of the surface over the 1 CN site). $Z_1$ is the distance of the lower atom from the surface. The contour lines are spaced by 0.5 eV. The $-2$ eV contour line is labelled at the top of the graph for reference.
Figure II.4  Contour plot for the $\text{H}_2$-W(001) potential (Surface II) with a parallel molecule-surface geometry (i.e. the $\text{H}_2$ molecule is parallel to the plane of the surface with its center of mass over the 1 CN site). $Z_{\text{c.m.}}$ is the distance of the $\text{H}_2$ center of mass from the surface. The contour lines are spaced by 0.5 eV. The $-2$ eV contour line is labelled at the top of the graph for reference.
Figure II.5  Contour plot for the H$_2$-W(001) potential (Surface II) with a perpendicular molecule-surface geometry (i.e. H$_2$ molecule is perpendicular to the plane of the surface over the 1 CN site). $Z_1$ is the distance of the lower atom from the surface. The contour lines are spaced by 0.5 eV. The $-2$ eV contour line is labelled at the top of the graph for reference.
Figure II.6  Contour plot for the H$_2$-Ni(100) potential with a parallel molecule-surface geometry (i.e. the H$_2$ molecule is parallel to the plane of the surface with its center of mass over the 1 CN site). Z$_{c.m.}$ is the distance of the H$_2$ center of mass from the surface. The contour lines are spaced by 0.5 eV. The $-2$ eV contour line is labelled at the top of the graph for reference.
Figure II.7  Contour plot for the H$_2$-Ni(100) potential with a perpendicular molecule-surface geometry (i.e. H$_2$ molecule is perpendicular to the plane of the surface over the 1 CN site). $Z_1$ is the distance of the lower atom from the surface. The contour lines are spaced by 0.5 eV. The $-2$ eV contour line is labelled at the top of the graph for reference.
Figure II.8  The effect of H$_2$ collision energy on the dissociative chemisorption of H$_2$ on Ni(100). The H$_2$ is in its ground rovibrational state and incident along the surface normal.
Figure II.9  $H_2(v,j) + \text{Ni}(100)$: The classical trajectory results of this work compared to mixed quantum-classical (Cruz and Jackson [34(c)]).
Figure II.10 The effect of initial rotational state of H₂ on the dissociative chemisorption of H₂ on Ni(100).
Figure II.11  A qualitative representation of the reduced potential used to elucidate the effects of rotation in gas phase reactions. The potential is for the coplanar gas phase reaction AB + C with zero impact parameter (AB is homonuclear).
Figure II.12 The effect of rotational alignment on the dissociative chemisorption in H₂ + Ni(100).
Figure II.13 The effect of H₂ collision energy on the dissociative chemisorption of H₂ on W(001) [Surface I]. The H₂ is in its ground rovibrational state and incident along the surface normal.
Figure II.14 The effect of $\text{H}_2$ collision energy on the dissociative chemisorption of $\text{H}_2$ on W(001) [Surface II]. The $\text{H}_2$ is in its ground rovibrational state and incident along the surface normal.
$H_2(0,j) + W(001)$, [Surface I]

Figure II.15 The effect of initial rotational state of $H_2$ on the dissociative chemisorption of $H_2$ on W(001) [Surface I].
Figure II.16 The effect of initial rotational state of H₂ on the dissociative chemisorption of H₂ on W(001) [Surface II].
Figure II.17 The affect of rotational alignment on the dissociative chemisorption of H$_2$ on W(001) [Surface I].

\[ H_2 (0,j) + W(001) \]
Surface I
\[ E_{\text{coll}} = 0.7 \text{ eV} \]

- ▲ $j = 2$
- ○ $j = 5$
- ■ $j = 8$
Table II.1  Parameters for the H$_2$-W(001) potential energy surface given in equations (1) through (8). Parameters are taken from reference 1(a).

<table>
<thead>
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<th><strong>Parameter</strong></th>
<th><strong>Value</strong></th>
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</tr>
<tr>
<td>$r_{01}$</td>
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</tr>
<tr>
<td>$\alpha_1$</td>
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<tr>
<td>$B$</td>
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Table II.2  Parameters for the H$_2$-Ni(100) potential energy surface given in equations (9) through (14). Parameters are taken from reference 4.

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<tr>
<td>$D_1$</td>
<td>4.7466 eV</td>
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<tr>
<td>$r_{01}$</td>
<td>7.41319 x $10^{-1}$ Å</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>1.97345 Å$^{-1}$</td>
</tr>
<tr>
<td>$\Delta_1$</td>
<td>0.05</td>
</tr>
</tbody>
</table>

| $D_0$     | 2.74 eV   |
| $\alpha_2 = \alpha_3$ | 1.25 Å$^{-1}$ |
| $z_0$     | 1.16 Å    |
| $\varepsilon$ | 0.0363     |
| $\delta$  | 0.15      |
| $\Delta_2 = \Delta_3$ | 0.2        |
CHAPTER III

A NOVEL ISOTOPE EFFECT IN HD + W(001) AT HIGH ENERGIES

Introduction

Recently there has been great interest in the microscopic study of chemical encounters at the gas-solid interface [1-28]. Most of these studies focus on low energy (below 1 eV) events important in catalysis [1-6]. A classic test case is the dissociative chemisorption of hydrogen on metal surfaces:

\[ \text{H}_2(g) + \text{S} \rightarrow 2\text{HS}, \]

(where S stands for surface) [5,6]. Such processes take place at energies well below the bond dissociation energy of the molecule, thus contributing to the catalytic nature of metal surfaces. We address reactions of this type in Chapter II.

However, in the past few years there has also been considerable research done on gas-surface collisions where the collision energy is much greater than the binding energy of the scattered species [7-22]. Amirav and Gerber and coworkers have studied the collision induced dissociation of \( \text{I}_2 \) scattered from chemically inert surfaces (surfaces where I-S is not an energetically favored product) both experimentally and theoretically [7-10] at energies in the range of 3-10 eV. In addition, the dissociative scattering of van der Waals (vdW) dimers and larger clusters [11-14, and Chapter I of this work] from surfaces has been investigated. Work has also been carried out on the scattering of molecular ions [15-20] and neutral molecules [21-22] from surfaces.
at very high energies (20 eV to several keV). All evidence indicates that these processes are impulsive in nature, involving mechanisms where translational energy is efficiently converted into energy along the reaction coordinate.

Other recent studies have demonstrated the importance of processes where a gas phase species collides with an adsorbed atom or molecule. For example, Ceyer and coworkers [23] have shown that the dissociation of methane physisorbed on Ni(111) is facilitated by bombardment with a beam of argon atoms. In addition, several recent molecular beam studies [24-26] have shown the existence of Eley-Rideal type processes in gas-surface reactions.

The suggestion that gas surface reactions proceeded by the direct “pickup” of chemisorbed species by gas phase molecules;

\[ A(g) + BS \rightarrow AB(g) + S, \]

was made by Eley and Rideal over 50 years ago [27]. However, for many years no direct experimental evidence of such reactions existed. Most gas-surface reactions were found to proceed via the Langmuir-Hinshelwood mechanism. In this process both reactants first chemisorb, become equilibrated with the surface, react and finally desorb from the surface.

In 1991 Kuipers et al [24] presented the first unequivocal experimental evidence of the Eley-Rideal mechanism. In that study, they observed the direct abstraction of protons from H covered Pt(111) by N(C\(_2\)H\(_4\))\(_3\)N molecules with with hyperthermal collision energies (2 and 9 eV). Subsequently, Zare and coworkers, in a combined experimental and theoretical study, demonstrated the direct “pick up” of relatively large hydrocarbon species adsorbed on a surface by polycyclic aromatic hydrocarbon ions. Most recently, Rettner [25] has reported evidence of the Eley-Rideal mechanism in a molecular beam study of the reaction of fast gas phase H (D) atoms with D (H) atoms chemisorbed on a metal surface to form gas phase HD.
In this we chapter address the reverse of the Eley-Rideal process, in which only one atom from a gas phase molecule is chemisorbed:

\[ \text{AB}(g) + S \rightarrow \text{AS} + \text{B}(g). \]  

This process, analogous to bimolecular gas phase reactions, has been termed "dissociative trapping" [28]. Energetically, for the HD + W(001) system, the dissociative trapping channel opens at energies well above the threshold for chemisorption but below that for collision induced dissociation. However, Stillinger and Weber predict it to be the major pathway for F₂ + Si(100) at low energies [29]. Dissociative trapping has been studied theoretically using classical trajectories [28,30]. It has also been treated quantum mechanically within the IOS approximation [31].

The focus of this work is on isotope effects we have observed in trajectory studies on the dissociative trapping of HD on W(001). In the solution phase, isotopic labelling of hydrogen has traditionally been of great use in elucidating reaction mechanisms [32]. More recently, isotope effects have been used in gas phase reactions (particularly those involving H₂ molecules) to explore the details of potential energy surfaces [33-35]. In particular, the effect of reactant energy on isotope branching has been investigated. One interesting finding from quasiclassical trajectory calculations [34] is that in exchange reactions of the type:

\[ \text{HD}(g) + \text{A}(g) \rightarrow \text{HA}(g) + \text{D}(g) \text{ or } \text{DA}(g) + \text{H}(g), \]  

where A is an atom, enhanced translation or vibration favors D atom abstraction, whereas increased rotational energy yields H atom abstraction. This characteristic of gas phase reactions has been termed the rotational isotope effect [34].

The primary goal of this work is to ascertain whether comparable trends exist in reactive molecule-surface scattering. The dissociative trapping of HD
(as opposed to dissociative chemisorption or collision induced dissociation) allows for two distinct outcomes depending on whether H or D is trapped on the surface. Therefore, the study of this process is a logical choice in the search for such isotope effects, which to our knowledge have not been investigated previously. Also, since mobile chemisorbed H atoms may play a crucial role in several catalytic processes [36], the ability to isotopically label these atoms presents exciting possibilities for the study of these reactions.

Calculations

The potential energy surface used to model the HD + W(001) system was the modified LEPS potential of McCreery and Wolken [37]. In this potential the metal surface is corrugated and rigid. Further details about the potential can be found by referring to either reference 37 or Chapter II of this work. The parameters used in this study are those of H2-W(001) Surface II from Chapter II.

Quasiclassical trajectory calculations [38] were used to solve the dynamics of the diatom-rigid surface system. Each trajectory was initiated with the diatom randomly positioned above the surface lattice and far enough from the surface so that the diatom-surface interaction was negligible. The initial center of mass velocity of the molecule was normal to the surface. The coordinates and momenta representing the initial quantum state of the diatom (v,ζ,mj) were chosen using the method of Porter et al [39]. The magnetic quantum number mj was chosen randomly between -j and j. Trajectories were terminated when they could be classified as having one of the following five outcomes:

1. no reaction,
2. collision induced dissociation (CID),
3. dissociative trapping (DT) of the D atom,
(4) dissociative trapping (DT) of the H atom, or
(5) dissociative chemisorption (DC).

In this chapter we concentrate on a comparison of translational and rotational energy isotope effects in the dissociative trapping of HD. In addition, we present the results of similar calculations using the molecules HT and H$^7$H (where $^7$H is a theoretical isotope of hydrogen with mass 7).

**Results and Discussion**

**Observations**

Figures III.1(a) and III.1(b) show the probability of each reactive outcome of the HD + W(001) reaction as a function of translational energy (Figure III.1(a)) and rotational energy (Figure III.1(b)). In both cases, as expected, dissociative chemisorption (DC) is the only allowable reactive channel at low energies. The probability of DC rises rapidly from threshold for both forms of reactant energy; although rotation is found to be slightly more effective than translation in promoting this process. A further increase in either translational or rotational energy results in the onset of dissociative trapping (DT) at a total energy of approximately 2 eV. In both cases, as the DT channel becomes accessible, the probability of chemisorption decreases. At still higher energies (around 5 eV) the threshold for collision induced dissociation (CID) is observed. The probability of CID increases at the expense of DT. In fact, although not shown in Figure III.1, the probability for DT decreased to 0.29 while that of CID increased to 0.57 for HD(v=0,j=0) by a collision energy ($E_{coll}$) of 15 eV.

Dissociative trapping of HD can occur via the trapping of either the H atom or the D atom. In Figures III.1(c) and III.1(d) we examine these separate channels explicitly. Figure III.1(c) shows that, at high translational energies, the trapping of H is preferred to the trapping of D. On the other hand, it is evident from Figure III.1(d) that rotational energy favors the trapping of D. Just as in the
gas phase, a rotational isotope effect is present, preferring a different channel than does translation. However, in contrast to the gas phase, the heavier atom is preferentially abstracted by rotation. We will explain these isotope effects below within the framework of the mechanism for dissociative trapping.

In Figure III.2(a) we show the probability of each reaction channel, with HD(\(v=0, j=0\)) and \(E_{\text{coll}} = 7\) eV, as a function of the initial geometry of the diatom above the surface. Here \(\xi_0\) is defined as the initial angle between the DH bond vector (D→H) and the surface normal. From this figure it is clear that chemisorption originates primarily from geometries with \(\xi_0\) near 90°. Furthermore, it is found that most CID and a sizeable portion of the DT also come from trajectories with near parallel initial geometries. However, Figure III.2(a) also shows that DT is more probable when the diatom is initially oriented nearly perpendicular to the surface. Examination of Figure III.2(b) establishes that DT tends to occur in a way such that the atom initially oriented away from the surface is trapped while the atom which strikes the surface first escapes. These results, showing the dependence of the reactive outcome on the initial geometry of a nonrotating diatom above the surface, are similar to those obtained by Baer and coworkers [30] in an earlier trajectory study.

However, the results shown in Figure III.2 are for nonrotating reactant diatoms. Obviously the initial orientation angle \(\xi_0\) is no longer useful in determining whether this mechanism for DT operates in rotationally excited collisions. However, the observation of individual trajectories for such cases reveals once more that the atom which collides first escapes, leaving the second atom trapped.

In Figure III.3 we present the kinetic energy distributions of the scattered atoms from both CID and DT. Figure III.3(a) displays the kinetic energy distribution in a case with high collision energy (HD(\(v=0, j=0\)) with \(E_{\text{coll}} = 7\) eV.).
We find that in this case dissociative trapping results in D atoms that are translationally hotter than the corresponding H atoms. However, Figure III.3(a) also shows that for this same case, the D and H atoms from collision induced dissociation scatter with equivalent energies. The kinetic energy distributions for scattered atoms in a case with high rotational energy ( HD\(v=0,j=29\) with \(E_{\text{coll}} = 0.7\text{eV}\) ) are shown in Figure III.3(b). In this case, as in the high collision energy case, the H and D atoms from collision induced dissociation scatter with similar energies. However, unlike the case with high \(E_{\text{coll}}\), the H atoms from dissociative trapping in this instance are found to be slightly hotter than the corresponding D atoms.

Figure III.4 contains the final scattering angle data for the scattered atoms from both the high collision energy and high rotational energy cases. In general, the scattering is highly nonspecular (the specular angle is 0°), peaking at a scattering angle between 30° and 60° with nonzero intensity out to scattering angles approaching 90°.

The distribution of intensity with scattering angle is an observable which provides direct evidence of the DT process itself, as well as the "translational" and "rotational" isotope effects. A comparison of the shaded regions representing the scattered H atoms (bottom panel) and D atoms (top panel) in Figure III.4(a) show that for high \(E_{\text{coll}}\) the number of scattered D atoms is greater than the number of the scattered of H atoms. Inspection of Figure 4(b) shows the opposite is true for high \(E_{\text{rot}}\). In each case this is evidence of the DT process, since if CID was the only source of scattered atoms H and D would be scattered with equal probability (note that the number of H atoms and D atoms produced by CID is equal in both Figure III.4(a) and III.4(b) ). Furthermore, the larger number of scattered D atom in Figure III.4(a) confirms the "translational"
isotope effect. Conversely, direct evidence for the "rotational" isotope effect is found in the larger number of scattered H atoms shown in Figure III.4(b).

Table III.1 shows the branching ratios of the probability of H trapping compared to the probability of heavy isotope trapping (where the heavy isotopes are D, T and 7H). The results in column I of this table show that for high E_{coll}, the "translational" isotope effect is enhanced by increasing the mass of the heavy isotope. Likewise, column II shows that at high rotational energy the rotational isotope effect is also enhanced by increasing the mass of the heavy isotope.

**Comparison to Previous Studies**

**Dependence on Initial Geometry** - As mentioned above, Figure III.2(a) shows that DC results primarily from initial geometries where the HD bond is nearly parallel to the surface. This result is not surprising since the parallel geometry resembles that of the transition state for chemisorption [37]. Less obvious perhaps is the finding that most CID and a large fraction of DT also result from near parallel initial geometries. Previous work on the scattering of van der Waals(vdW) clusters from chemically inert surfaces [11,13 and Chapter I of this work] found that dissociation was caused chiefly by compression of the vdW bond, with the bond being broken by the recoil. Hence, dissociation was found to come predominantly from trajectories with near perpendicular initial geometries. The difference between those studies and our findings lies in the reactive nature of the H₂-W(001) potential. Since the parallel geometry is strongly preferred energetically on a surface where dissociative chemisorption is possible, the potential exerts a torque, rotating non-parallel geometries towards \( \zeta = 90^\circ \). At this angle, the bond can stretch more easily. In fact, the observation of individual trajectories shows that in both CID and DT the atoms
are already well separated by the time they collide with the repulsive part of the potential and are, therefore, easily separated.

Kinetic Energy Distribution of Scattered Atoms - In general, the kinetic energy distributions of scattered atoms presented in Figure III.3 are unimodal. This stands in contrast to the bimodal distribution observed by Gerber and Elber [8] for the CID of I₂ scattered from a surface which did not allow for the chemisorption of I atoms. In that work the most distinctive features in the kinetic energy distribution of the scattered atoms were a "fast atom peak" and a "slow atom peak". The potential energy surface used in the present work, however, has a strongly exothermic atom-surface chemisorption channel. Therefore, after the diatom bond is broken the slower atoms would tend to be trapped on the surface, perhaps suppressing the slow atom peak.

Scattering Angle Distribution - In an earlier study of the scattering of N₂-rare gas vdW dimers from chemically surfaces [11 and Chapter I of this work] we found that the resulting N₂ monomers were scattered at highly nonspecular angles with no monomer intensity at the specular angle (0°). As mentioned previously, dissociation of these dimers involved a compression of the vdW bond leading to a "hard" collision between the monomers. This collision provided an impulse along the vdW bond which scattered the monomers at nonspecular angles.

We have obtained similar scattering angle distributions for the scattered atoms resulting from dissociative trapping and collision induced dissociation in the HD-W(001) system (Figure III.4). However, in this case there is no hard collision between the H and D atoms since, as stated above, the HD bond is considerably stretched before the molecule collides with the surface. A likely explanation for this is that as the diatom approaches the surface and is rotated towards the transition state for chemisorption, some of the potential energy is
converted into kinetic energy along the reaction coordinate (the HD bond) parallel to the surface. This nonvertical contribution to the velocity leads to nonspecular scattering.

**Mechanism**  

It appears that both DT and CID occur via the same general mechanism. In the first step the diatom bond is broken. This occurs essentially before the diatom strikes the surface. Next, after the diatom-surface collision, the separated atoms are left to either escape or become chemisorbed on the surface. In CID both atoms escape, whereas in DT only one atom is able to escape. The results in Figure III.3 imply that when the atoms have comparable energies after dissociation they can both escape from the surface and CID occurs. However, in DT the atom which escapes the surface takes a disproportionate fraction of the available energy, leaving its partner with insufficient energy to escape.

It is perhaps easiest to explain how the inequitable distribution of energy leading to dissociative trapping comes about by describing the process for a homonuclear diatom such as H₂ in its rovibrational ground state. When the H₂ is far from the surface, the velocity of each of its atoms is essentially the center of mass velocity of the molecule. As the diatom approaches the surface, it experiences a torque, tending to rotate it towards a geometry parallel to the surface. Although the angle ζ never reaches 90°, the diatom bond begins to stretch as it approaches this configuration. As stated above, this converts some of the diatom's potential energy into energy along the reaction coordinate. In the limit that this energy were released suddenly, as in photodissociation, it is clear that the two H atoms would move away from each other, conserving their center of mass. Therefore, vector addition of this extra velocity to the center-of-mass velocity of the approaching H₂ would tend to accelerate the atom closer to
the surface downwards towards the surface while slowing down the approach of the second atom. The magnitude of the velocity of each of the scattered atoms normal to the surface will determine whether or not that atom will escape after colliding with the surface. If this component of the velocity is large enough the atom will escape, if not it will be trapped. Therefore, the energetic atom colliding first is more likely to have enough energy to escape. On the other hand, it is more probable that the second atom will have too little energy to escape and will be trapped on the surface.

For near perpendicular geometries the atom which hits the surface first carries a larger fraction of the energy after the diatom-surface collision. Therefore, DT is more likely to occur in such cases. On the other hand, for near parallel geometries it is much more likely that both atoms will scatter with comparable energy, leading to CID.

The Isotope Effects

The Translation Isotope Effect - The isotope effects in the dissociative trapping of HD shown in of Figure III.1(c) and III.1(d) can be explained within the above mechanism. In the case of a ground state light-heavy type molecule such as HD(v=0,j=0) travelling with a given center-of-mass collision energy, the heavy atom will carry more translational energy than the light atom. For example, in the case of a non-vibrating molecule AB (A is the light atom, B is the heavy atom) with collision energy $E_{\text{coll}}$, the atom A carries energy $E_{\text{coll}}[M_A / M_{AB}]$ and atom B carries $E_{\text{coll}}[M_B / M_{AB}]$ (where $M_A$ and $M_B$ are the masses of atoms A and B respectively, and $M_{AB} = M_A + M_B$). In this case one would expect the heavy atom A to carry more energy than the lighter atom B after dissociation. This is supported by Figure III.4(a) which shows that the overall kinetic energy of scattered D atoms tends to be more than that of scattered H atoms in the case of high $E_{\text{coll}}$. Hence, when the D atom strikes first, it is already
carrying a larger fraction of the translational making it even more likely that the H atom will be trapped.

One would expect that the "translational" isotope effect would be enhanced as the ratio $M_A/M_B$ is decreased. Column I of Table III.1 shows this to be the case in HD + W(001). The trapping of H goes from being 1.7 times more likely than the trapping of D to 4.3 times more likely than the trapping of D, as the heavy isotope of hydrogen goes from D to $^7$H.

We also find that when the less energetic H atom strikes first the likelihood of both atoms escaping increases. This is illustrated in Figure III.2(a) which shows that although DT is less probable, when the H atoms strikes the surface first CID is, in fact, more probable in this instance.

These results support the findings of an earlier work on dissociative trapping [30] in which molecules with several different mass combinations were studied. In that work, it was found that for HCl and HI (more extreme example of light-heavy than examined here) the probability of the heavy atom being trapped was zero. This was due to the fact that the heavy Cl and I atoms always carried enough energy to escape the chemisorption well. Also, since the H atom carried such a small fraction of the collision energy, the collision induced dissociation channel was found to be closed out to very high collision energies (> 100 eV).

The Rotational Isotope Effect - However, in the case of rotationally excited HD, however, the situation is quite different. When the rotational energy is high compared to $E_{\text{coll}}$ the H atom carries more kinetic energy than the D. For example, given the same rigid light-heavy molecule AB mentioned above with rotational energy $E_R$, atom A would carry $E_R[M_B / M_{AB}]$ and atom B would carry $E_R[M_A / M_{AB}]$. This is supported by Figure III.3(b), which shows that for high rotational energy scattered H atoms tend to be more energetic than scattered D.
atoms. Also, as the rotational energy becomes very large compared to $E_{\text{Coll}}$, the approaching molecule can be pictured as the heavy atom moving slowly towards the surface with the lighter atom rotating rapidly around it. This increases the likelihood that the lighter atom will hit the surface first. Since the light atom carries more energy and is also likely to collide with the surface first, one would expect that the trapping of the heavy atom would be favored for high rotational energy. Also, one might also expect that, as in the "translational" isotope effect, the "rotational" isotope effect would also be enhanced as $M_A/M_B$ decreases. This is supported by column II of Table III.1 which shows that the trapping of H is just as likely as the trapping of D for HD but is 60 percent less likely for $H^7H$.

**Conclusions**

We have carried out quasiclassical trajectory calculations for reactive scattering in HD + W(001) from low to intermediate total energy. We find two pronounced isotope effect in the dissociative trapping channel: Translational excitation favors the trapping of the H atom whereas rotational excitation favors the trapping of the D atom. These isotope effects are just the opposite of those observed in the analogous gas phase reaction, HD(g) + A(g) (where A is an atom) [31]. A mechanism for dissociative trapping in which the HD bond is essentially broken before collision with the surface has been proposed. This mechanism is supported by observation of both the scattering angle and product energy distributions.
REFERENCES


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Figure III.1 (a) and (b) Probability of each reactive outcome as a function of $E_{\text{coll}}$ (a) and $E_{\text{rot}}$ (b). (c) and (d) Probability of each distinct outcome in the dissociative trapping of HD as a function of $E_{\text{coll}}$ (c) and $E_{\text{rot}}$ (d). The lowest energy point on each plot (a-d) corresponds to HD($v=0,j=0$) with $E_{\text{coll}} = 0.70$ eV. $E_{\text{tot}}$ is the sum of the internal and c.m. translational energy of the diatom. Increasing $E_{\text{tot}}$ in Figures 1(a) and (c) corresponds to increasing translational energy, whereas increasing $E_{\text{tot}}$ in Figures 1(b) and (d) corresponds to increasing rotational energy. The total energy in (b) and (d) was limited because HD was found to dissociate at rotational energies above 4.9 eV.
Figure III.1

![Graphs showing rotational and translational probabilities with energy values.](Image)

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Figure III.2  (a) Probability of each reactive outcome as a function of the initial orientation of the diatom with the surface for HD($v=0,j=0$) with $E_{\text{coll}} = 7.0$ eV. (b) The probability of each distinctive outcome for the dissociative trapping of HD (initial conditions are the same as in (a)).
Figure III.2

(a)CID
○ Total DT
■ DC

(b)D Trapped
○ H Trapped

Probability vs. \( \zeta_0 \) / degrees
Figure III.3  Energy distributions of scattered H and D atoms resulting from the
dissociative trapping (DT) and collision induced dissociation (CID)
of HD for (a) high $E_{\text{coll}}$ (HD($\nu=0,j=0$) with $E_{\text{coll}} = 7.0$ eV ) and (b)
high $E_{\text{rot}}$ ( HD($\nu=0,j=29$) with $E_{\text{rot}} = 4.7$ eV and $E_{\text{coll}} = 0.7$ eV ).
Figure III.4  Scattering angle distribution for the same trajectories as in Figure III.3.
<table>
<thead>
<tr>
<th></th>
<th>I. Translation</th>
<th>II. Rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD</td>
<td>1.7 ± 0.2</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>HT</td>
<td>2.1 ± 0.3</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>H(^7)H</td>
<td>4.3 ± 0.8</td>
<td>0.40 ± 0.07</td>
</tr>
</tbody>
</table>

Table III.1 Branching ratios for dissociative trapping (probability of hydrogen trapping compared to probability of heavy isotope trapping) for high translational energy (Column I) and high rotational energy (column II). In all cases E\(_{\text{tot}}\) (diatom translational energy plus internal energy) was 4.5 eV. Column I corresponds to HD\((v=0,j=0)\) with E\(_{\text{coll}}\) = 4.3 eV. Column II corresponds to HD\((v=0,j)\) with E\(_{\text{coll}}\) = 0.7 eV where j was adjusted to make E\(_{\text{tot}}\) = 4.5 eV.
CHAPTER IV

CLUSTER CATALYZED CHEMISORPTION OF H₂ ON Si(111)(1X1)

Introduction

Due to the importance of processes such as molecular beam epitaxy, chemical vapor deposition and the etching of semiconductor surfaces in the microelectronics industry, the interactions of gas phase species with silicon surfaces have become the subject of intensive research [1-18]. The reaction of molecular hydrogen with silicon surfaces serves as a prototypical case of such interactions and has become one of the most studied gas-semiconductor systems [10-18]. In this chapter, we consider the effect on the dissociative chemisorption of H₂ on Si(111)(1X1) of solvating an H₂ molecule in an argon microcluster.

The study of cluster-surface impact phenomena has been a field of considerable interest for more than 20 years [19-30]. Several studies have been performed on the scattering of atomic and molecular van der Waals (vdW) clusters from metal surfaces at hyperthermal energies [19-25]. In general, these studies, as well as the results presented in Chapter I of this work, show that clusters fragment upon impact with the surface, displaying dynamics very different from those observed in monomer-surface scattering. Furthermore, the impact of large cluster ions with surfaces has recently become an active area of study [26-29]. It is found that beams of large cluster ions show smaller space-charge effects than do beams of atomic or molecular ions, with each cluster

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delivering a relatively large amount of energy to a localized region on a surface. It is hoped that this work will find applications in fields such as surface cleaning, precision machining, surface sputtering [26-27] and the epitaxial growth of preferentially oriented thin films [28-29].

In a recent molecular dynamics study [31], Landman and coworkers showed that gas phase attachment reactions involving either [Na4Cl3]⁺ or [Na14Cl12]⁺ and a Cl⁻ anion can be catalyzed by solvating the sodium chloride fragment in an argon cluster, which serves as a local heat reservoir. Subsequently, Cleveland and Landman [30] reported that the impact of a relatively large cluster of 561 argon atoms with a surface results in the formation of a shock wave-like region within the cluster. They proposed that this environment may be used to catalyze chemical reactions. Since that work, Whetten and coworkers [32] have presented the first experimental evidence of reactions in cluster-surface collisions. Specifically, in the scattering of alkali fluoride clusters from silicon at hyperthermal energies (0.1 to 0.5eV per atom), they observe the reaction:

\[ \text{[Na}_n\text{F}_{n-1}]^+ \rightarrow \text{[Na}_n\text{F}_{n-2}]^{2+} + \text{F}^-(s), \]  

(where F⁻(s) is a surface fluoride species) when n was greater than 30.

Recently we presented what we believe to be the first theoretical study of the catalysis of a chemisorption reaction via cluster-surface collision [33]. In that work we investigated the possibility of enhancing the chemisorption of H₂ on Si(111)(1X1) by dissolving the H₂ in a small noble gas cluster. The purpose of this chapter is to provide a more detailed analysis of that work, and also to introduce some additional findings.
Calculations

The Cluster Potential and Geometries

The potential representing the vdW bonds of the Ar\(_n\)H\(_2\) heterocluster was pairwise additive between the two H atoms and n argon atoms with the form:

\[
V_{\text{vdW}} = \sum_{i=1}^{n} \sum_{j=1}^{2} V_{\text{Ar-H}}(r_{ij}) + \sum_{i=1}^{n} \sum_{k>i}^{n} V_{\text{Ar-Ar}}(r_{ik}),
\]  

(2)

where \(V_{\text{Ar-H}}\) and \(V_{\text{Ar-Ar}}\) are Lennard-Jones (6-12) potentials representing the Ar-H [34] and Ar-Ar [23] interactions respectively. The argon atom-hydrogen atom potential is given by:

\[
V_{\text{Ar-H}} = 4 \varepsilon_{\text{Ar-H}} \left[ \left( \frac{\sigma_{\text{Ar-H}}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\text{Ar-H}}}{r_{ij}} \right)^{6} \right],
\]  

(3)

where \(r_{ij}\) is the distance between Ar atom i and H atom j. The argon-argon interaction is given by:

\[
V_{\text{Ar-Ar}} = 4 \varepsilon_{\text{Ar-Ar}} \left[ \left( \frac{\sigma_{\text{Ar-Ar}}}{r_{ik}} \right)^{12} - \left( \frac{\sigma_{\text{Ar-Ar}}}{r_{ik}} \right)^{6} \right],
\]  

(4)

where \(r_{ik}\) is the distance between Ar atom i and Ar atom k. The vdW potential parameters for equations (3) and (4) are presented in Table 1.

Minimum energy geometries for Ar\(_n\)H\(_2\) clusters with \(n = 1, 2, 4, 5, 7\) and 12 were obtained with the H\(_2\) held at its equilibrium bond distance. The minimum energy geometries for \(n = 1\) and 2 are trivial. However, as the cluster size increases the number of stable minima is expected to rise dramatically [35] and some sort of numerical minimization technique is required to efficiently locate the most stable configurations. In this work the simulated annealing algorithm [36] was used for this purpose. The simulated annealing method in general, and how it was applied to the Ar\(_n\)H\(_2\) system are detailed in Appendix 2.

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The Cluster-Surface Interaction

The cluster-surface (C-S) potential used to model the interaction of \( \text{Ar}_n\text{H}_2 \) with \( \text{Si}(111)(1\times1) \) had the form:

\[
V_{\text{C-S}} = V_{\text{H}_2\text{-S}} + V_{\text{Ar-S}},
\]

(5)

where \( V_{\text{H}_2\text{-S}} \) represents the \( \text{H}_2 \)-silicon surface potential and \( V_{\text{Ar-S}} \) represents the interaction between the argon atoms and the silicon surface.

The \( \text{H}_2 \)-Surface Potential - The \( \text{H}_2 \)-silicon surface interaction, \( V_{\text{H}_2\text{-S}} \), is that used by Raff and Thompson and coworkers [11,15] in their studies of reactive processes involving \( \text{H}_2 \) at the \( \text{Si}(111)(1\times1) \) surface, and is given by:

\[
V_{\text{H}_2\text{-S}} = V_{\text{H}\text{-H}} + V_{\text{H-S}},
\]

(6)

where \( V_{\text{H}\text{-H}} \) is the \( \text{H}_2 \) intramolecular potential and \( V_{\text{H-S}} \) is the interaction between the \( \text{H} \) atoms and the silicon surface. The \( V_{\text{H}\text{-H}} \) term consists of a Morse interaction which is attenuated by a hyperbolic switching function as the diatom approaches the surface:

\[
V_{\text{H}\text{-H}} = D_{\text{H-H}} \left[ \exp\left(\frac{-2\beta_{\text{H-S}}(R - R_s)}{\beta_{\text{H-S}}}ight) - 2 \exp\left(\frac{-\beta_{\text{H-S}}(R - R_s)}{\beta_{\text{H-S}}}ight) \right] \tanh\left(\alpha Z_c\right),
\]

(7)

where \( R \) is the H-H interatomic distance and \( Z_c \) is the distance of the \( \text{H}_2 \) center of mass above the surface. The parameters for equation (7) are given in Table IV.1.

The silicon lattice used in this work is that employed in references 11 and 15. It consists of 95 atoms representing the first three layers of silicon. Of these atoms, 25 are in the first layer, with 35 each in the second and third layers. The Si-Si bond length was taken to be 2.352 Å. In Figure IV.1 we show pictorial representations of two views of the model \( \text{Si}(111)(1\times1) \) surface slab.

The interaction between the \( \text{H} \) atoms and the silicon surface, \( V_{\text{H-S}} \) and is a pairwise sum between \( \text{H} \) and the silicon atoms of the first two layers of the lattice. It is written as:
\[
V_{i-j} = \sum_{i=1}^{26} \left( \sum_{i=1}^{26} V_{ij} + \sum_{k=26}^{60} V_{ik} \right) \times \left\{ \frac{a + b \tanh \left[ \omega (R - R_0) \right]}{a + b} \right\},
\]
where \( V_{ij} \) and \( V_{ik} \) are Morse interactions between the H atoms and the first and second layers of silicon atoms respectively. These are given by
\[
V_{ij} = D \left\{ \exp \left[ -2\beta (r_{ij} - r_s) \right] - 2 \exp \left[ -\beta (r_{ij} - r_s) \right] \right\},
\]
where \( r_{ij} \) is the distance between H atom i and Si atom j in the first layer of the surface, and by
\[
V_{ik} = D' \left\{ \exp \left[ -2\beta' (r_{ik} - r_s') \right] - 2 \exp \left[ -\beta' (r_{ik} - r_s') \right] \right\},
\]
where \( r_{ik} \) is the distance between H atom i and Si atom k in the second layer of the surface. The hyperbolic switching function in equation (8) attenuates these interactions as the H-H bond is formed. The parameters for equations (8), (9) and (10) are also given in Table IV.1.

The \( \text{H}_2-\text{Si}(111)(1\times1) \) potential energy surface described above has a 0.182 eV barrier to dissociative chemisorption, the process by which an \( \text{H}_2 \) molecule dissociates to form two chemisorbed H atoms:
\[
\text{H}_2(\text{g}) + \text{Si}(111) \rightarrow 2\text{H-Si}(111),
\]
and a 2.52 eV barrier for recombinative desorption (the reverse process). The minimum energy path to dissociative chemisorption occurs when the \( \text{H}_2 \) molecule approaches the surface directly above one of the top layer Si atoms, with the H-H axis parallel to the surface. Although the adsorption of atomic hydrogen is allowed with this potential, the adsorption of intact \( \text{H}_2 \) is not. This is in accordance with experimental results for the reaction of \( \text{H}_2 \) with \( \text{Si}(111) \) [12]. Therefore, the collision of \( \text{H}_2 \) with the surface will always result in either reflection of intact \( \text{H}_2 \) or dissociative chemisorption.
The Argon-Surface Potential - The argon-surface potential is pairwise additive between the Ar atoms of the cluster given by and the Si atoms of the first two layers of the surface. It is given by:

\[ V_{Ar-Si} = \sum_{i=1}^{n} \sum_{j=1}^{50} V_{Ar-Si}(r_{ij}), \] (12)

where \( V_{Ar-Si} \) is a Lennard-Jones (6-12) potential representing the interaction between an Ar atom and a silicon atom in the lattice [37]. This interaction is given by:

\[ V_{Ar-Si} = 4 \varepsilon_{Ar-Si} \left( \frac{\sigma_{Ar-Si}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{Ar-Si}}{r_{ij}} \right)^{6}, \] (13)

where \( r_{ij} \) is the distance between Ar atom \( i \) and Si atom \( j \). The parameters used in equation 13 are presented in Table IV.1.

The Dynamics

We used molecular dynamics simulations to model the scattering of \( Ar_nH_2 \) microclusters (\( n = 1, 2, 4, 5, 6, 7 \) and 12) from the Si(111)(1X1) surface. The trajectories were initiated with the clusters in the minimum energy geometries found from simulated annealing. For the dynamics the \( H_2 \) molecule was given internal energy corresponding to its (v=0, j=0) state. The coordinates and momenta corresponding to this initial state were determined using the method of Porter et al. [38].

One potential danger in working with classical simulations is the fact that energy can "leak" out of a bound molecule with a high-frequency vibration, leaving the molecule with less than the quantum mechanical zero point energy [39]. If sufficient energy is lost, this could even lead to evaporation of the cluster by the loss of one or more Ar atoms. The observation of individual trajectories
showed that, in this case, the internal energy of the H\(_2\) molecule did not leak out into the Ar atom motion quickly enough to evaporate the cluster or invalidate our assumption that H\(_2\) remained in its (v=0, j=0) state prior to colliding with the surface.

At the start of each trajectory the cluster was randomly oriented in space with the H\(_2\) center of mass randomly placed above the central unit cell of the lattice surface (see Figure IV.1(a)). The trajectory was initiated with the cluster incident along the surface normal and far enough above the surface so that the cluster-surface interaction was negligible. Hamilton's equations of motion [40] were integrated with time until the trajectory could be classified as reactive (the H-H bond length large and both H-surface bond lengths small) or nonreactive (the H-H bond length small and both H-surface bond lengths large). The fifth-order Gear integration technique [41] was used since the time scales of the H-H motions was much shorter than that of other motions in the system. Each run consisted of from 100 to 200 trajectories. The total energy was conserved to better than 1 part in 10\(^5\) using a variable size time step.

**Ar\(_n\)H\(_2\) Microcluster Geometries**

**Absolute Minima**

**Results** - The lowest energy geometries obtained for the Ar\(_n\)H\(_2\) clusters (n ≥ 4) using simulated annealing are shown in Figures IV.2(a-d) and Figure IV.3(a). It is expected that the number of stable configurations for Ar\(_n\)H\(_2\) will increase dramatically with n. For example, Hoare and McInnes [35] found no fewer than 988 stable configurations for a cluster of 13 Lennard-Jones atoms. Therefore, even after simulated annealing, it is impossible to be entirely certain that Figures IV.2(a-d) and Figure IV.3(a) represent the absolute minima for Ar\(_n\)H\(_2\). Nonetheless, it is encouraging to note that these structures correspond to the polytetrahedral minimum energy structures found by Hoare and Pal [42]
for clusters of Lennard-Jones atoms, except here the H$_2$ molecule replaces an atom in the corresponding atomic cluster.

Thus, if we assume that the H$_2$ molecule is indistinguishable from the argon atoms; Ar$_4$H$_2$ is a trigonal bipyramid, Ar$_5$H$_2$ is a tripyramid consisting of three connected tetrahedrons, Ar$_6$H$_2$ is a pentagonal bipyramid with the H$_2$ in the five membered ring, and Ar$_7$H$_2$ is a pentagonal bipyramid with an argon atom added to one of the trigonal faces. Following the growth sequence from Figure IV.2(a) (n = 4) to Figure IV.2(c) (n = 7) one finds that each successive minimum energy structure can be obtained by adding an argon atom to a trigonal face on the preceding cluster.

In Figure IV.3(a) we show the lowest energy structure determined for Ar$_{12}$H$_2$. This cluster is found to have an icosahedral structure, consisting of a central monomer surrounded by 12 "solvating" monomers occupying equivalent sites on the outer shell. This structure for Ar$_{12}$H$_2$ is obtained by following the same packing scheme described above. The addition of an argon atom to each trigonal face on one side of the pentagonal bipyramid shown in Figure IV.1(c) plus one argon to cap this newly formed pentagon leads to the structure shown in Figure IV.2(a).

Discussion - It has been shown computationally that the optimal packing for finite numbers of Lennard-Jones atoms follows a noncrystallographic motif characterized by concentric icosahedral shells [43]. Filled shell structures, referred to as Mackay icosahedra [44], corresponding to clusters of 13, 55, 147, 309... monomers show enhanced stability. The structure for Ar$_{12}$H$_2$ shown in Figure IV.3(a) is that of the first Mackay icosahedron. Experimental evidence of icosahedral structures in small argon clusters [45-46] and in small clusters of CH$_4$ and N$_2$ [46] has been obtained in electron diffraction studies on jet expansions of these substances. These same studies show that crystalline
structure does not manifest itself until cluster sizes of several thousand monomers. Also, compelling experimental evidence has been provided showing that the Mackay icosahedron structures represent especially stable structures in ionized rare gas microclusters [47] and rare gas clusters doped with a single metal atom ion [48]. It is believed that the clusters in such cases consists of a charged center surrounded by neutral atoms.

Examination of each of the absolute minimum energy structures (Figures IV.2(a - d) and Figure IV.3(a ) shows that the H_2 preferentially occupies a site of minimal coordination. It should be noted that the Ar-Ar (0.0123 eV) interaction is approximately 60 percent stronger than the total Ar-H_2 (0.00762 eV) interaction. Hence, for these geometries there is a propensity for minimization of the total Ar-Ar potential, leaving the H_2 occupying an external site with lower coordination. For example, in the minimum energy geometry for Ar_{12}H_2 the central monomer is coordinated to each of the 12 other monomers in the outer shell. On the other hand, each monomer in the outer shell is coordinated to 6 other monomers, the central monomer and 5 of the other outer shell monomers. Hence, by placing an Ar atom in the central position of the icosahedron, the number of the stronger Ar-Ar interactions is maximized. This is in qualitative agreement with predictions made by Perara and Amar [49] as to the favored geometries for rare gas microsolution clusters where the solvent-solvent interaction is stronger than the solvent-solute interaction.

An Alternative Structure for Ar_{12}H_2

In Figure IV.3(b) we show an alternative stable minimum for the Ar_{12}H_2. In this case the H_2 molecule occupies the central position in the icosahedron. The binding energy of this vdW complex is found to be 0.4750 eV, as compared to 0.5009 for the most stable structure ( Figure IV.3(a )). The vdW binding
energy for this isomer of Ar\textsubscript{12}H\textsubscript{2} is 0.0259 eV lower than that of the lowest energy isomer, the equivalent of three Ar-H\textsubscript{2} bonds or two Ar-Ar bonds.

**Reactions of Unclustered H\textsubscript{2} with Si(111)(1X1)**

In Figure IV.4 we show the probability of dissociative chemisorption for unclustered (n = 0) H\textsubscript{2} in its rovibrational ground state on Si(111)(1X1) as a function of collision energy. There is no reaction for H\textsubscript{2} energies less than 0.4 eV. After the reaction threshold at 0.4 eV, however, reactivity rises rapidly until it reaches a plateau of about 78 percent by a collision energy of 0.6 eV.

As mentioned above in the description of the H\textsubscript{2}-Si(111)(1X1) potential energy surface, the collision of H\textsubscript{2} molecules with the silicon surface always results in either reflection of intact H\textsubscript{2} or dissociative chemisorption. It was also stated that the the lowest barrier to dissociative chemisorption is 0.182 eV [11]. However, the dynamic threshold for dissociative chemisorption in Figure IV.4 occurs at a collision energy of around 0.4 eV. This is explained by the fact that the 0.182 eV threshold for reaction is for a H\textsubscript{2}-surface collision geometry in which the diatom axis is parallel to the surface [11]. If the H\textsubscript{2} collides with the surface in a geometry other than parallel to the surface as will most often be the case, the barrier to chemisorption is increased. Therefore, the 0.4 eV threshold for reaction shown in Figure IV.4 is due to a dynamical effect, which results from the low probability of the H\textsubscript{2} molecule colliding with the surface in the optimal geometry for chemisorption.

**The Reaction Ar\textsubscript{n}H\textsubscript{2} Microclusters with Si(111)(1X1)**

Clusters with Minimum Energy Geometries

**The Effect of Cluster Size and Velocity** - Shown in Figure IV.5 is the H\textsubscript{2} chemisorption probability for Ar\textsubscript{n}H\textsubscript{2} + Si(111)(1X1), at a cluster velocity of 3.1 km s\textsuperscript{-1}, as the number of argon atoms is increased. This collision velocity corresponds to a collision energy of 0.1 eV for lone H\textsubscript{2}. From the previous
figure it is clear that unclustered H₂ does not chemisorb at this collision energy. In Figure IV.5 we see that there is little reaction for clusters up to \( n = 4 \). However, a further increase in cluster size results in a dramatic rise in the chemisorption probability: For the icosahedral Ar₁₂H₂ cluster, the reaction probability is as high as that for a collision energy of 0.5 eV for unclustered H₂. Thus, the chemisorption of H₂ on Si(111)(1X1) is enhanced by dissolving H₂ in an argon microcluster with the reaction probability increasing dramatically with the size of the argon "solvent" cluster.

In Figure IV.6 we show the probability of H₂ chemisorption for ArₙH₂ as a function of cluster size for two different collision velocities, (a) 4.4 km s⁻¹ and (b) 4.8 km s⁻¹. These velocities correspond to collision energies of 0.20 and 0.25 eV respectively unclustered H₂. Once again, the reaction probability increases with cluster size. However, for both of these higher collision velocities the reaction probability is approximately 25 percent by a cluster with \( n = 7 \), as compared to 10 percent for the same cluster size with a collision velocity of 3.1 km s⁻¹. Thus, the H₂ becomes more reactive as the cluster-surface collision becomes more energetic.

Figure IV.7 shows the probability of H₂ chemisorption for Ar₁₂H₂ as a function of collision velocity. We present data for collision velocities ranging from 0.98 to 5.4 km s⁻¹. These velocities correspond to H₂ center of mass collision energies from 0.01 to 0.3 eV. The reaction probability increases monotonically from approximately 4 percent at a collision velocity of 0.98 km s⁻¹ and plateaus at approximately 33 percent by a collision velocity of 3.1 km s⁻¹.

**Cluster Surface Collision Dynamics** - Several theoretical studies of cluster-surface scattering have been carried out [23-26,28-30] (see also Chapter I of this work). All reveal the same underlying mechanism: The lower layers of the cluster recoil from the surface and collide with the upper layers.
which are still impinging upon the surface, creating a 'piling up' effect [30]. Hence, cluster translational energy vertical to the surface is transferred into internal motion. This leads to multiple impulsive collisions between the monomers within the cluster and, ultimately, cluster fragmentation. Also, monomers in the lower layers of the cluster may undergo multiple collisions between the surface and the upper layers of the cluster. As a result energy can be transferred from the upper layers to the monomers in contact with the surface. In fact, in their study of the collision of large argon clusters from an NaCl surface, Cleveland and Landman [30] report that the 'piling up' of successive cluster layers results in a region of very high kinetic energy capable of damaging the crystal.

The Reaction Mechanism - In Figure IV.5, which shows the probability of H₂ chemisorption as a function of cluster size, the 0.1 eV of translational energy carried by the H₂ is well below the observed threshold for dissociative chemisorption (0.4 eV) shown in Figure IV.4. However, at this collision velocity the total energy of a given cluster is \((2n + 0.1)\) eV, where \(2n\) eV is the translational energy of the "solvent" argon atoms. Obviously, each cluster represented in Figure IV.5 has more than enough energy to overcome the barrier to dissociative chemisorption. However, in order to react some energy must be transferred from the argon "solvent" to the H₂. The same is true for the trajectories represented in Figure IV.6(a) where the H₂ center of mass collision energy is 0.20 eV, and in Figure IV.6(b) for an H₂ center of mass collision energy of 0.25 eV.

Figures IV.2 and IV.3 show that ArₙH₂ microclusters favor configurations where the H₂ molecule occupies a position of low coordination, on the exterior of the cluster. Hence, in the case of the lowest energy cluster geometries
(Figures IV.2 and IV.3(a)), the H₂ has more or less uninhibited access to the surface during cluster-surface collisions where the H₂ faces towards the surface. Also, according to the cluster-surface collision mechanism described above, once the H₂ molecule recoils from the surface it can gain a great deal of energy via collisions with the upper layers of the cluster. Furthermore, the opportunity for multiple collisions increases the probability that the H₂ will collide with the surface in a geometry favorable for chemisorption.

From the observation of individual trajectories we have found that reaction does indeed occur when the cluster-surface collision geometry is such that the H₂ is on the "bottom" of the cluster. We illustrate this in Figures IV.8 and IV.9. In Figure IV.8 we show time dependent pictures of a typical reactive trajectory viewed from the side. Figure IV.9 contains pictures of the same trajectory, this time viewed from above, so that it is easier to see the separation of the H atoms after chemisorption. In Figure IV.10 we show the distance of the H₂ center of mass from the surface (Z_H₂), the H-H bond distance (r_H₂) and the H₂ center of mass momentum of this trajectory as a function of time.

Figure IV.10(a) shows that the H₂ collides with the surface at approximately 3.8 ps. This is accompanied by a sudden increase in the H₂ center of mass momentum (see Figure IV.10(c)). Thus, the H₂ becomes energetic enough to overcome the reaction barrier and chemisorbs. The breaking of the H-H bond is illustrated in Figure IV.10(b). These events occur between the picture in Figure IV.8(b) and that in Figure IV.8(c). It is clear that in Figure IV.8(b), the H₂ has not yet collided with the surface. In Figure IV.8(c) we see that the argon "solvent cluster" has begun to pile up on the H₂ molecule. During this time cluster translation energy, primarily from the argon atoms, is transferred to the internal modes of the cluster. This leads to cluster fragmentation, as illustrated in Figures IV.8(e) and IV.9(d). Another result of
this process is that the H$_2$ molecule gains enough energy to overcome the barrier to dissociative chemisorption. This is reminiscent of Ceyer's work [50] in which physisorbed species were induced to overcome a barrier to chemisorption by bombardment with noble gas atoms; in our case the bombarding species are carried *in situ*.

Figure IV.11 contains time dependent pictures of a typical nonreactive trajectory. In Figure IV.12 we show both the distance of the H$_2$ center of mass from the surface (Z$_{H_2}$), and the H$_2$ center of mass momentum of this trajectory as a function of time. We see that in this case the H$_2$ is located on the "upper hemisphere" of the cluster. Hence, the argon "solvent cluster" blocks the H$_2$ molecule from the surface. In fact, from Figure IV.12(a) it is clear that the H$_2$ molecule does not come closer than 10 a.u. from the surface, as opposed to a closest distance of less than 3 a.u. for the reactive case (see Figure IV.10(a)). Also, even though the H$_2$ molecule once again gains energy from the cluster during the fragmentation process, the momentum is away from the surface and cannot be used for reaction.

This explains the plateau in the reaction probability as a function of collision velocity observed in Figure IV.7 for Ar$_{12}$H$_2$. For collision velocities greater than 3.1 km s$^{-1}$ reaction depends mainly on the cluster-surface collision geometry; i.e. whether or not the H$_2$ is "caged" at the surface by the argon atoms. Hence, even though the cluster-surface collisions become more energetic with increased collision velocity, no reaction will occur if the argon "solvent cluster" blocks the H$_2$ from the surface. From our results it would seem that this occurs approximately 67 percent of the time for the lowest energy isomer of Ar$_{12}$H$_2$.  

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The Effect of Cluster Geometry in $\text{Ar}_{12}\text{H}_2 + \text{Si}(111)(1\times1)$

In the case of the more stable of the two isomers (Figure IV.3(a)) the $\text{H}_2$ occupies one of the twelve essentially equivalent outer sites of the icosahedron. On the other hand, in the case of the less stable $\text{Ar}_{12}\text{H}_2$ isomer (Figure IV.3(b)), the $\text{H}_2$ is at the center of the icosahedron surrounded by the 12 "solvent" argon atoms. In what follows we shall refer to results pertaining to the lowest energy $\text{Ar}_{12}\text{H}_2$ geometry as the "$\text{H}_2$ outside" case, while those pertaining to the less stable geometry will be referred to as the "$\text{H}_2$ inside" case.

**Results** - In Figure IV.13 we show the probability of dissociative chemisorption of $\text{H}_2$ at a collision energy of 3.1 km s$^{-1}$, for the two isomers of $\text{Ar}_{12}\text{H}_2$ depicted in Figure IV.3. The probability of reaction is greater than 30 percent for the "$\text{H}_2$ outside" case. On the other hand, in the "$\text{H}_2$ inside" case the reaction probability falls to less than 1 percent.

In Figure IV.14 we show the probability of dissociative chemisorption for the case where the $\text{H}_2$ is located "inside" of the cluster, as a function of cluster collision velocity. We display data for collision velocities ranging from 2.2 to 6.2 km s$^{-1}$. These velocities correspond to center of mass collision energies of 0.05 to 0.4 eV for lone $\text{H}_2$. We also include the corresponding data for the "$\text{H}_2$ outside" case, as displayed in Figure IV.7. The threshold for reaction for the "$\text{H}_2$ inside" case occurs at a collision velocity of 3.1 km s$^{-1}$. The threshold is followed by a monotonic rise in the reaction probability as the collision velocity is increased.

We also wish to note here that at a collision velocity of 6.2 km s$^{-1}$, included in the reactive trajectories for the "$\text{H}_2$ inside" isomer are two trajectories that could not be classified as dissociative chemisorption. In one case, although the H-H bond was broken only one of the H atoms chemisorbed to the surface, with the second returning to the gas phase. This process has

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been termed dissociative trapping (see Chapter III of this work). In the second instance, the H-H bond was broken and both H atoms returned to the gas phase. This process is known as collision induced dissociation (see also Chapter III). For the scattering of lone H$_2$ from the Si(111)(1X1) surface, these two reaction channels become available only at high energies (greater than 1 eV).

**Discussion** - The threshold velocity of 3.1 km s$^{-1}$ for "H$_2$ inside" isomer stands is much higher than that of the "H$_2$ outside" isomer (less than 0.98 km s$^{-1}$). In the latter case the reaction probability is already 33 percent by a collision velocity of 3.1 km s$^{-1}$. This disparity in reactivity is not due to a difference in the basic reaction dynamics of the two isomers. In general, the cluster-surface collision dynamics are the same in each case: Upon impact, cluster translational energy is converted into internal energy with the H$_2$ molecule gaining energy from the argon "solvent".

However, in the case where the H$_2$ is located "inside" of the cluster, the H$_2$ molecule is surrounded by an essentially isotropic solvent shell of argon atoms. Hence, for this case there is no cluster-surface collision geometry for which the H$_2$ has uninhibited access to the surface (recall that for the "H$_2$ outside" case at this collision velocity, the reaction proceeds with 100 percent efficiency for cluster-surface collisions where the H$_2$ is between the argon "solvent" cluster and the surface). Therefore, in order for reaction to occur in the "H$_2$ inside" case the H$_2$ molecules must obtain enough energy to first "break through" the "solvent shell" of argon, and then overcome the barrier to dissociative chemisorption. Hence, H$_2$ is much more likely to react when it occupies a site on the outside of the argon atom "shell".
Conclusions

In this chapter we have shown, using molecular dynamics simulations, that the activated dissociative chemisorption of H₂ on Si(111)(1X1) can be facilitated by dissolving the H₂ in an argon microcluster. We have also shown that the reactivity of such microclusters depends on whether the reactive species occupies a site of minimal coordination (i.e. on the “outside” of the cluster), or a site of high coordination (i.e. “inside” of the cluster).

From these results we suggest that one possible technique for enhancing activated chemisorption is to first physisorb the reactant onto a cluster *en route* to the surface, perhaps by a cluster 'pickup' technique or just in nozzle expansion [51], leading to a cluster catalyzed reaction.

In these calculations we have made two simplifying assumptions: The surface was held rigid during the collision; and we neglected the possibility of electronic excitation of the solid. While a realistic treatment of surface motion is important in correctly describing energy and momentum transfer [30], we believe that it is less crucial to the outcome for this particular reactive system. Study of individual trajectories reveals that there is a high likelihood of reaction if the H₂ is successfully caged at the surface. The actual magnitude of the momentum imparted by the cluster is then less important than the fact that some momentum is available to overcome the activation energy to reaction. Also, it has been shown [11] that the chemisorption probability for lone H₂ on a dynamic Si(111)(1X1) surface increases with surface temperature. Therefore, surface motion may actually enhance the chemisorption of H₂ from ArₙH₂ clusters as the impact of the cluster locally increases the surface temperature.

It is rather less clear to evaluate the significance of possible electronic excitations. From the above discussion, it is apparent that they will affect our findings only if they dramatically increase the activation energy for dissociative
chemisorption. On the contrary, it seems more likely that electronic excitations would make the solid appear more metallic, reducing the activation energy; most H$_2$/metal dissociative chemisorption activation energies [52] are lower than the 0.18 eV of H$_2$/Si(111) [11].

In further work, we intend to treat surface motion more realistically. Calculations with larger clusters are already underway, as are investigations of the effects of cluster and surface temperature on the reaction.
REFERENCES


(a) Top View

3.834 Å

(b) Side View

Figure IV.1  Two views of the model Si(111)(1X1) surface slab. In each view the top layer Si atoms are blackened for easy identification.  (a) The top view, looking down along the surface normal. The second row atoms of the center surface unit cell are shaded. (b) A view from the side.
Figure IV.2 Minimum energy geometries for ArₙH₂ (ₙ = 4, 5, 6, and 7) as determined by simulated annealing (V_{vdW} is the total vdW potential while V_{H₂-Ar} is the contribution of the H-Ar interactions): (a) Ar₄H₂ (V_{vdW} = -0.0953 eV, V_{H₂-Ar} = -0.0222 eV), (b) Ar₅H₂ (V_{vdW} = -0.1335 eV, V_{H₂-Ar} = -0.0223 eV), (c) Ar₆H₂ (V_{vdW} = -0.1786 eV, V_{H₂-Ar} = -0.0287 eV), (d) Ar₇H₂ (V_{vdW} = -0.2168 eV, V_{H₂-Ar} = -0.0278 eV).
Figure IV.3 Two isomers of the Ar$_{12}$H$_2$ cluster, (a) the lowest energy geometry shown in Figure IV.1 ($V_{vdw} = -0.5009$ eV, $V_{H_2$-Ar} = -0.0425$ eV), and (b) a less stable isomer where the peripheral H$_2$ molecule in Figure IV.3(a) exchanges places with the central Ar atom ($V_{vdw} = -0.4750$ eV, $V_{H_2$-Ar} = -0.0793$ eV).
Figure IV.4  Probability of dissociative chemisorption for $H_2(v=0,j=0) + Si(111)(1\times1)$ as a function of the $H_2$ center of mass collision energy, $E_{\text{coll}}$.  

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Figure IV.5 Probability of $H_2$ dissociative chemisorption for $Ar_nH_2$ as a function of cluster size. Cluster collision velocity is 3.1 km s$^{-1}$ which corresponds to $H_2$ center of mass collision energy of 0.1 eV.
Figure IV.6  Probability of H$_2$ dissociative chemisorption for Ar$_n$H$_2$ as a function of cluster size for two different collision energies. Cluster collision velocities are (a) 4.4 km s$^{-1}$ and (b) 4.9 km s$^{-1}$ which correspond to H$_2$ center of mass collision energies of 0.20 eV and 0.25 eV respectively.
Figure IV.7  Probability of H₂ dissociative chemisorption for Ar₁₂H₂ as a function of collision velocity. Data are shown for collision velocities of 0.98, 2.0, 2.6 and 3.1 km s⁻¹ which correspond to H₂ center of mass collision energies of 0.01, 0.04, 0.07 and 0.1 eV respectively.
Figure IV.8 Time dependent "snapshots" of a reactive $\text{Ar}_{12}\text{H}_2 + \text{Si}(111)(1\times1)$ trajectory viewed from the side. The cluster collision velocity is $3.1$ km s$^{-1}$. 

(a) $t = 0.167$ ps
(b) $t = 0.319$ ps
(c) $t = 0.387$ ps
(d) $t = 0.434$ ps
(e) $t = 0.505$ ps
Figure IV.9  Time dependent "snapshots" of a reactive trajectory viewed from above the surface. The trajectory is the same as that depicted in Figure IV.8. This figure gives a clearer view of the H$_2$-Si(111) dissociative chemisorption process.
Figure IV.10  The distance of the $H_2$ center of mass from the surface ($Z_{H_2}$), the $H$-$H$ bond distance ($r_{H_2}$), and the center of mass momentum of $H_2$ as a function of time for the trajectory depicted in Figures IV.8 and IV.9. The times which are "tagged" correspond to pictures in the previous two figures.
Figure IV.11  Time dependent "snapshots" of a nonreactive trajectory. Cluster collision velocity is 3.1 km s$^{-1}$.
Figure IV.12 The distance of the $H_2$ center of mass from the surface ($Z_{H_2}$), and the center of mass momentum of $H_2$ as a function of time for the trajectory depicted in Figure IV.11. The times which are "tagged" correspond to pictures in the previous two figures.
Figure IV.13 Probability of H\textsubscript{2} dissociative chemisorption for the two Ar\textsubscript{12}H\textsubscript{2} isomers depicted in Figure IV.6 for a cluster collision velocity is 3.1 km s\textsuperscript{-1} which corresponds to H\textsubscript{2} center of mass collision energy of 0.1 eV.
Figure IV.14 Probability of H₂ dissociative chemisorption for the higher energy Ar₁₂H₂ isomer (filled circles). The solid line is a best fit curve to these data. The results for the lower energy isomer from Figure IV.7 are included for comparison (open triangles). The dashed line is a best fit curve to this data.
Table IV.1  Potential parameters for the Ar$_n$H$_2$-Si(111)(1x1) system with references.

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APPENDIX A

THE FIRST ALIGNMENT RATIO FOR DIATOM ROTATION

In this appendix we briefly discuss the concept of the first alignment ratio for diatom rotation as it is applied to diatom-surface scattering. In diatom-surface scattering, alignment data give information as to the plane of diatom rotation above the surface. In inelastic diatom-surface scattering the alignment of the scattered molecules has shed much light on the dynamics of such processes [1-4]. It has also been suggested that the rotational alignment of incident diatoms will have a strong effect on reactivity in dissociative chemisorption [5-6].

A rotating molecule, either incident upon or scattered from a surface, possesses an angular momentum vector \( \mathbf{J} \). This vector makes an angle, \( \chi \), with some fixed measurement axis, \( \hat{n} \), usually taken to be the surface normal. In the absence of a magnetic field, the probability distribution of \( \chi \) for a large number of molecules, \( n(\chi) \), is even on \( \cos \chi \) and, therefore, can be expressed as an expansion in the Legendre polynomials:

\[
n(\cos \chi) = \sum_{i= \text{even}} \left( i + \frac{1}{2} \right)^{-1} b_i P_i(\cos \chi),
\]

(1)

where \( b_i \) and \( P_i \) are the \( i \)th expansion coefficient and \( i \)th Legendre polynomial respectively. The \( i \)th expansion coefficient is, therefore, given by:
\[ b_i = \left( i + \frac{1}{2} \right) \int_{-1}^{1} n(\chi) P_i(\cos \chi) \, d\cos \chi, \]  

Experimentally it is possible to measure the first alignment ratio, \( b_2/b_0 \) [1-2], which provides very useful information on the spatial distribution of the angular momentum vector, \( \mathbf{J} \). A \( b_2/b_0 \) value of 0 corresponds to an unaligned distribution of \( \mathbf{J} \). On the other hand, nonzero first alignment ratios correspond to aligned distribution.

The first alignment ratio has a maximum value of 5 and a minimum value of -2.5. A value of 5 for \( b_2/b_0 \) indicates that \( n(\chi) \) lies exclusively at \( \chi = 0 \), corresponding to rotation in a plane parallel to the surface. Such rotation has been termed "helicoptering" [4]. On the other hand, a large negative value for \( b_2/b_0 \) indicates that \( n(\chi) \) lies predominantly near \( \chi = \frac{\pi}{2} \). This corresponds to rotation in a plane perpendicular to the surface. Such rotation has been termed "cartwheeling" [4]. Examples of "cartwheeling" and "helicoptering" diatoms are illustrated in Figure A.1. In practice, a perfectly aligned distribution of \( \mathbf{J} \) (all "helicoptering" or all "cartwheeling") is seldom encountered. However, a large positive value of \( b_2/b_0 \) indicates a propensity for "helicoptering", while a large negative value indicates a predominance of "cartwheeling."
REFERENCES


Figure A.1  Illustration showing "helicoptering" and "cartwheeling" molecules above a surface. The surface lies in the (x,y) plane. The z axis serves as the surface normal.
APPENDIX B

SIMULATED ANNEALING

Introduction

Simulated annealing allows for the optimization of problems of very large scale [1-3]. In particular, it has become a popular method for minimizing many dimensional functions [2-3]. In this appendix we briefly discuss the application of this numerical method to the minimization of the potential energy for a small assembly, or cluster, of atoms.

The potential energy function for even a relatively small number of atoms may contain a large number of local minima, corresponding to stable configurations. For example, Hoare and McInnes [4] identified no fewer than 988 structurally distinct minima for a cluster of 13 atoms bound by a pairwise additive Lennard-Jones potential. Therefore, the identification of the global (absolute) minimum energy configuration for even this relatively simple system would appear to be quite a task.

Many standard minimization techniques employ a strategy based on "iterative improvement" [2]. Such methods proceed quickly and directly "downhill" to a minimum. However, this is not necessarily the global minimum of the system. Obviously, such an approach is inappropriate for determining the absolute minimum energy structure of an atomic cluster. Simulated annealing, on the other hand, offers an effective method for seeking out the global minimum of such a system.
Real Annealing

The technique of real annealing is used to prepare well characterized, defect-free crystals. In this process the material to be annealed, a metal for example, is heated up and then slowly cooled. At high temperatures the metal is liquid and its atoms move freely with respect to one another. It can, therefore, can assume many configurations. If the system is cooled slowly enough, as the atoms lose their thermal mobility they will align themselves and eventually become locked in place, forming a pure crystal [1]. This represents the minimum energy for this system (the global minimum). On the other hand, if the metal is rapidly cooled or “quenched”, the atoms become locked into an amorphous or polycrystalline state which is higher in energy than the pure crystal [1]. This represents a local minimum for the metal atom system. As we shall see below, the simulated annealing algorithm mimics real annealing as it occurs in nature.

The Metropolis Monte Carlo (MMC) Procedure

The probability distribution of energy in a thermally equilibrated system at a given temperature, $T$, is given by the Boltzmann probability distribution:

$$P(E) \propto \exp\left(-\frac{E}{kT}\right),$$

(1)

where $P(E)$ is the probability of being in an energy state $E$ and $k$ is the Boltzmann constant. Thus, for a thermalized assembly of atoms there is a nonzero probability, albeit small, for the existence of structures with relatively high energies. Accordingly, it is always a possible for the system to “climb” in energy from a more stable to a less stable configuration.

Almost 30 years ago, Metropolis and coworkers [4] introduced a simple algorithm, applicable to the simulation of a collection of atoms in thermal
equilibrium at a given temperature, which makes use of this physical phenomenon. One starts with an assembly of atoms in some initial configuration. In each step of the algorithm, a randomly selected atom is given a small random displacement. The resulting change in the potential energy of the system, \( \Delta E \), is then calculated. If \( \Delta E \leq 0 \), the displacement is accepted and the new configuration is used to initiate the next step. If \( \Delta E > 0 \), the probability that the move will be accepted is given by:

\[
P(\Delta E) = \exp\left(-\frac{\Delta E}{kT}\right).
\]  

The decision to accept or reject the new configuration is then made by comparing \( P(\Delta E) \) to a random number between 0 and 1. If \( P(\Delta E) \) is greater than the random number, the move is accepted and the new configuration is used to initiate the next step. If \( P(\Delta E) \) is less than the random number, the move is rejected. In this case, the old configuration is used to initiate the next step. As a consequence of equation (2), the energies of the series of selected configurations will show a Boltzmann distribution.

**The Simulated Annealing Algorithm**

In this section we describe how the simulated annealing process is applied to minimizing the potential energy of a small cluster of atoms. The algorithm is initiated by generating a starting geometry for the cluster and giving it a "temperature". The initial temperature should be relatively high so that even configurations with high potential energy are easily accessible. This is analogous to "melting" the cluster. The MMC procedure is applied until a prescribed number of cluster configurations are accepted at the current temperature (here \( \Delta E \) from equation (2) corresponds to the difference in potential energy between the current configuration and the new "candidate").
Next, after the prescribed number of acceptances has been made at a higher temperature, the cluster is assigned a new, slightly lower, temperature. The MMC technique is then applied at this new temperature, using the final accepted configuration from the previous temperature as the starting geometry. The same procedure is repeated a number of times, using a slightly lower temperature at each time. This is, of course, analogous to slowly lowering the temperature in real annealing. As the temperature is lowered, higher energy configurations become less probable, and the atoms will tend to settle into a configuration corresponding to a minimum. However, as a consequence of the MMC sampling method, there is always a chance that the system might "climb" out of a local minimum in the energy potential function. Eventually the temperature becomes very low and no new configurations are accepted. If the temperature was lowered sufficiently slowly, there is a good chance that the final configuration will represent the absolute minimum energy structure of the cluster (Rigorously, if the cooling is done adiabatically -infinitely slowly- one is guaranteed to global minimum).

**Interpretation of Results**

Clearly, an infinitely slow cooling process is not possible. Therefore, although simulated annealing is well suited for finding the global minimum of a system such as a cluster of atoms, a single run does not guarantee the absolute minimum. In fact one can never be absolutely certain, particularly for a relatively large number of atoms, that the absolute minimum energy cluster configuration has been obtained.

There are, however, certain steps that one can take to become reasonably certain of the results. One helpful practice is to consult the literature concerning minimization studies on similar systems, if available. This may provide some information as to the general nature of the structure being sought.
More importantly, though, one must carry out the simulated annealing procedure a number of times for a single cluster. The starting geometry, the magnitude of the random displacement, the "cooling" schedule and the number of acceptances required at each temperature should be varied from run to run. If the same configuration consistently shows up as the lowest energy structure, one can be reasonably certain that it represents the absolute minimum.

**Concluding Remarks**

In this appendix we have presented an overview of the simulated annealing process and how it can be used to minimize the potential energy of a cluster of atoms. We have not, however, provided any specifics as to the optimal choices for the "cooling" schedules, initial geometries, prescribed number of acceptances, or the random displacement. These choices will likely vary greatly from cluster to cluster, depending on the cluster size and potential energy function. However, a few trial runs with a given cluster will usually give one a good idea on how to optimize the annealing scheme for that system.
REFERENCES


COMPREHENSIVE LIST OF REFERENCES


