

Title	Dynamics of Hydrogen-Solid Surface Reactions
Author(s)	Dino, Wilson Agerico Tan
Citation	大阪大学, 1999, 博士論文
Version Type	VoR
URL	https://doi.org/10.11501/3155367
rights	
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

https://ir.library.osaka-u.ac.jp/

The University of Osaka

# Dynamics of Hydrogen-Solid Surface Reactions

甲688-2

Orientational Effects on the Dissociative Adsorption, Inelastic Scattering, and Associative Desorption Dynamics of Hydrogen on Copper and Palladium Surfaces

1998

## Wilson Agerico Tan Diño

傅耀華

大阪大学大学院工学研究科応用物理学専攻 Department of Applied Physics Graduate School of Engineering Osaka University

## Dynamics of Hydrogen-Solid Surface Reactions

Orientational Effects on the Dissociative Adsorption, Inelastic Scattering, and Associative Desorption Dynamics of Hydrogen on Copper and Palladium Surfaces

## 1998

## Wilson Agerico Tan Diño

## 傅耀華

大阪大学大学院工学研究科応用物理学専攻

Department of Applied Physics Graduate School of Engineering Osaka University

## Contents

1	Introduction			
	1.1	Why Hydrogen?	2	
	1.2	Why Dynamical Calculations?	3	
	1.3	Why this Study?	4	
2	The	e Model System	13	
	2.1	Rigid Surface	14	
		2.1.1 The 1-Dimensional Activation Barrier	15	
		2.1.2 The Orientationally Anisotropic Potential Barrier and the Ef-	10	
		fective Molecular Bond-Length for a Rigid Surface	16	
		2.1.3 The Model Hamiltonian for a Rigid Surface	18	
	2.2		20	
		2.2.1 The Orientationally Anisotropic Potential Barrier and the Ef-	90	
		Iective Molecular Bond-Length for a Dynamic Surface	20	
		2.2.2 The Model Hamiltonian for a Dynamic Surface	Z3	
3	Rot	ational Effects in the Dissociative Adsorption and Inelastic		
	Sca	ttering Dynamics of $D_2/Cu(111)$	<b>25</b>	
	<b>3.</b> 1	Rigid Surface	25	
		3.1.1 Steering & Energy Transfer Effects	25	
		3.1.2 Incidence Energy Dependence	33	
		3.1.3 Isotope Effects	34	
	3.2	Dynamic Surface	36	
		3.2.1 Surface Recoil Effect	39	
	3.3	Steering, Energy Transfer, and Surface Recoil Effects	43	
4 Rotational Effects		ational Effects in the Associative Desorption Dynamics of		
	$D_2/$	Cu(111)	47	
	4.1	Consistency between Dissociative Adsorption and Associative De-		
		sorption Results	47	
	4.2	Rotational Alignment & Dynamical Quantum Filtering	50	
	4.3	Isotope Effects	56	
5	Rot	ational Effects in the Dynamics of Hydrogen on a Pd Surface	61	
	5.1	Rotational Effects in the Dissociative Adsorption Dynamics	61	
		5.1.1 Steering and Energy Transfer Effects	64	
		5.1.2 Isotope Effects	66	
	5.2	Rotational Effects in the Associative Desorption Dynamics	67	

	5.2.1	Rotational Alignment & Dynamical Quantum Filtering	67
6	Summary,	Conclusions, and Further Discussions	69
Re	References		
A	Acknowledgements		
Li	List of Related Publications		

# Chapter 1 Introduction

There is a long standing dream in the surface-science community to develop a material science of *heterogenous catalysis* (catalysis by powdered solids) [1]. The motivation is plain and simple. Hundreds of billions of yens in world economy are being generated by catalytic chemistry. If it were possible to gain a detailed, atomic-level understanding of surface reactions, then it might be possible to design less expensive, more effective catalytic substrates. Thus, it can be said that, one of the most exciting challenges of present-day surface science is the task of developing a detailed picture of surface reactions. This would involve understanding the intra- and inter-molecular motions of the reactants, as they undergo changes at a surface, and understanding the related issues of energy requirements, energy flow, and energy disposal for these microscopic interactions. Studies directed at describing atomic and molecular motion, and the relation between molecular motion and energy exchange throughout a surface process, such as chemisorption, physisorption, or scattering, define the field of surface dynamics. The descriptions acquired from studies of surface dynamics can range from simple conceptual models, which yield insights into qualitative aspects of molecular interactions, to detailed theories, which can provide more quantitative information about the dynamical process involved. To make any headway in understanding such surface reactions, the most fundamental surface reactions must be understood. One such reaction which has been, and is still being, extensively studied is the interaction of a diatomic molecule with a surface.

When diatomic molecules, prepared in a certain initial quantum mechanical state, interact with metal surfaces, a number of processes can occur, depending on the initial conditions. Some may be adsorbed as molecules, or as dissociated atoms, which may then be absorbed into the metal. Some may undergo dissociative scattering, *i.e.*, atomic fragmentation, with the products (fragmented/dissociated atoms) going back to the gas phase. Some may undergo elastic scattering (diffraction). Inelastic scattering via excitations of the molecular internal degrees of freedom (*e.g.*, rotation and/or vibration), or excitation of surface phonons and/or surface electron-hole pairs, may also occur. And after undergoing dissociative adsorption, the adsorbed atoms/molecules and desorb. In Fig. 1.1 we show a summary of the possible processes that may occur.

In this thesis, we shall mainly discuss the dynamics involved in dissociative adsorption and associative desorption, which represent the initial and the final stages in any reaction. DISSOCIATIVE ADSORPTION is the initial process by which we can



Figure 1.1. A schematic diagram of the several reactions that may occur when a diatomic molecule, prepared in a certain initial quantum mechanical state, interacts with a metal surface. The coordinates  $(X, Y, Z, \theta, \phi)$  give the location of the center-of-mass, and the polar and azimuthal orientations of the impinging diatomic molecule with respect to some reference point.  $(\nu_i, J_i, m_i, m_s)$  correspond to the initial vibrational, rotational, azimuthal, and spin quantum states of the impinging diatomic molecule, respectively.  $\Theta_i$  and  $\Theta_f$  correspond to the incidence and scattering angle of the diatomic molecule with respect to the surface normal, before and after a certain reaction occurs. The coordinates  $(x_j, y_j, z_j)$  give the location of the j-th contituent atom of the diatomic molecule after a certain reaction, e.g., dissociative adsorption or interaction with a photon  $(h\nu)$  of light, occurs.

utilize the surface as a catalyst, or medium, and initiate the reaction of two reactants that may otherwise even be, normally, too stable to interact with each other. ASSOCIATIVE DESORPTION, on the other hand, is the means by which we could harvest the resulting products of the reaction from the surface. In particular, we concentrate on the dissociative adsorption and associative desorption dynamics of hydrogen at copper and palladium surfaces.

## 1.1 Why Hydrogen?

Hydrogen is probably the most important of all atoms both for its abundance in the universe and for its theoretical interest. It is the only stable neutral two-body system, and its energy levels  $[cm^{-1}]$  can be calculated with an accuracy far higher than for any other element (currently of the order  $10^{-11}$ ). In addition, atomic hydrogen possesses a rich spectrum of resonances ranging from the radiofrequency to the ultraviolet frequency and is thus a fertile ground for experimentalists. Several of its absorption resonances are particularly narrow and thus very suitable for metrology. For these reasons the hydrogen atom has always played a central role in the development of modern physics since, by performing measurements of its energy level separations, one is able to make precise tests of current theories. (For more details regarding the role of hydrogen in modern physics and metrology, cf., e.g., [2].)

Furthermore, the understanding of how hydrogen interacts with metal surfaces is of broad interest. From a practical (technological) point of view (cf., e.g, [3-5]), the interactions of hydrogen with solids are influential in a number of industrial processes (e.g., heterogenous catalysis, material processing (hydrogen firing), purification of hydrogen by sorption or permeation, and fabrication of electronic devices), and in energy and power systems (e.g., fuel cells, nuclear reactors (tritium containment)). The ability of hydrogen to alter the mechanical properties of metals to the point of rendering them unreliable is an outstanding technological problem [6,7]. Interactions with certain materials lead to severe degradations in the mechanical (embrittlement, stress corrosion cracking), electrical, and magnetic properties of those materials. In the case of hydrogen-assisted cracking, in which crack initiation and propagation are controlled by a combination of stress and the presence of hydrogen, there is a relationship between the requisite stress and hydrogen-concentration: More hydrogen can reduce the failure stress. From an *environmental* point of view, with WATER as the only EMISSION from hydrogen combustion, hydrogen is very attractive as an alternative POWER SOURCE of the future, with materials that readily adsorb hydrogen as potential fuel storage devices (cf., e.g, [8,9]). From an academic point of view, hydrogen is the simplest possible adsorbate. Thus, an understanding of how hydrogen behaves when it approaches and subsequently comes into contact with a solid surface should give the most fundamental view of gas-surface reaction.

## **1.2** Why Dynamical Calculations?

The main trend in the study of gas-surface reaction some 40 years ago was towards kinetics [10-12], i.e., the study of how external macroscopic variables (e.g., temperature, pressure, and relative concentrations of the reactants) influence the overall reaction rate. It was the kinetic behavior of reactants near solid surfaces that was the focus for studying the chemically active species with surfaces. It was not that people then were not wondering as to why some molecules will stick to some surface intact, some will undergo fragmentation, some never at all (cf., e.g., [13-15]). It was simply not possible then to compare state-resolved theoretical predictions with kinetic data obtained by experiments because of the vast degree of averaging required to convert cross-sections into rate constants. However, with a number of diverse advances both in the experimental and theoretical fields, it is now possible to gain a more *microscopic* view of gas-surface interactions, where one can focus attention on the detailed atomic/molecular motions that characterize an elementary reaction, *i.e.*, the *dynamics* of the process. With the advent of sophisticated laser preparation and detection schemes (e.g., laser spectroscopy), combined with ultra-high vacuum (UHV) technology, it is now possible to perform experiments that can measure state specific information of molecules. Unfortunately, even though current experimental methods enable the exact motion of the nuclei in a reaction to be followed [16], there are still some microscopic details that remain inaccessible to direct investigations (e.g., time-dependence of the charge state of reacting species, correlated motion of a small cluster of atoms, etc.). And quantum mechanics tells us that it will always be *impossible* to follow the behavior of a molecule, as it interacts with the surface, without compromising the outcome. On the other hand, even though it is possible to write the exact Hamiltonian to describe the coupled electronic and nuclear motions as a reaction evolves, it is frequently impossible to find a solution, and the heart of the theoretical method is to make a simplified calculation, amenable to solution, that will contain the essential physics of the problem. Dynamical calculations, using as input data from both theoretical and experimental studies, can be made to model the experimental problem and, in a way, allow investigation of areas not accessible to experimentalists and other theorists. The results of these dynamical calculations may then be compared with the many available experimental data on this system (gas-surface interaction system), and provide us with a means to gauge just how close we are to having the important details of this system at our grasp.

#### 1.3 Why this Study?

The question of which forms of energy can best promote activated processes is central to the field of surface reactions. One important goal of this field is then to determine which physical factors (e.g., degree of freedom) most affect the outcome of potentially reactive collisions. Such detailed, atomic-level understanding of surface reactions should be of great value in optimizing reaction conditions and in controlling reaction yields. Furthermore, as mentioned earlier, it might permit the design of less expensive, more effective, novel catalytic substrates much needed in the industry [1]. Numerous studies, both theoretical and experimental, have been done to understand the energetic requirements and energy disposal in elementary reactions. Although most of these works are concerned with gas-phase reactants [17, 18], recent developments in theoretical and experimental techniques have made it possible to, also, examine the dynamics of gas-surface reactions [19,20], principally the process of activated dissociative chemisorption. And over the years, the chemisorption of hydrogen on copper surfaces has become a benchmark for the study of gas-surface interaction dynamics, particularly in developing a dynamical description of activated adsorption [10, 11, 21-23].

Experiments (cf., e.g., [10,11] and further references found therein) using seeded molecular-beam scattering and state-resolved time-of-flight (TOF) measurements of desorption, have studied the detailed dependence of the dissociation probability on the translational, vibrational, and rotational degrees of freedom and on surface temperature. From these experiments, we now know that dissociation of hydrogen on the low index surfaces of Cu is hindered by a considerable energy barrier. This means that a certain amount of energy must be fed to the translational degree of freedom of the hydrogen molecule before dissociative adsorption on a Cu surface could occur (cf., [10, 11] and references found therein). The dependence of the sticking probability on the angle of incidence of the molecular beam has also been measured. For Cu surfaces, normal energy scaling is found to be a good approximation [10,24], suggesting that only the component of the momentum perpendicular to the surface is effective in promoting dissociation. This is usually interpreted as implying that the surface appears to be flat to the dissociating molecule. Studies have also



Figure 1.2. Experimental rotational state j-dependent adsorption probabilities for D<sub>2</sub> in the vibrational ground state. The curves were obtained by plugging-in experimental data of Michelsen *et al.* [10,30,31] into their proposed functional form for the sticking coefficient, and assuming a j-independent normalization factor (A = 1) [31]. The gas phase rotational constant of D<sub>2</sub> is  $B \approx 3.8$  meV. From [36].

shown that the vibrational energy of incoming hydrogen molecules always promotes dissociation on the low index surfaces of Cu. And for a fixed initial (vibrational, rotational, and translational) state of the impinging hydrogen molecule, increasing the surface temperature slightly promotes dissociation for incidence energies a little lower than the effective energy barrier, and slightly hinders dissociation for incidence energies a little higher than the effective energy barrier, without changing the energetic location of the inflection point of the corresponding adsorption probability curves [25]. Furthermore, we also know that the dissociation of hydrogen on Cu is an orientation-dependent process, *i.e.*, hydrogen molecules oriented parallel to the Cu surface dissociate more easily compared to perpendicularly oriented ones [26,27]. However, it is only now that we are beginning to understand how rotational energy or the molecular rotational degree of freedom actually influences hydrogen dissociation.

Recently, time-of-flight (TOF) distributions for hydrogen molecules associatively desorbing from Cu(111) could be determined rotationally state resolved (cf., [28-32] and references found therein). Earlier desorption measurements for H<sub>2</sub> and D<sub>2</sub> from Cu(110) and Cu(111) by Kubiak *et al.* [28] indicate that the mean rotational energy in desorption associated with the detected low rotational states j of the hydrogen molecules is slightly less than that appropriate to the surface temperature ( $k_BT_S$ ) (rotational cooling). The measured rotational state distributions appear to have slightly enhanced populations at low rotational state j. Schröter *et al.* [29] later observed a rather strong rotational cooling for the H<sub>2</sub> on Pd(100) system. And



Figure 1.3. Experimental results for the rotational state j-dependent sticking probability curves for H<sub>2</sub> on Pd(111) for fixed translational energies  $E_t$ . Arrows point to the corresponding minimum for each curve. The curves were obtained by replotting the experimental data of Gostein and Sitz (Table II of [39]). The statistical uncertainties for the sticking probabilities were omitted in the figure for clarity. The corresponding incidence energies  $E_t$ , and the location of the minimum for each curve  $j_{min}$ , are as follows—

 $\Box: E_t = 55 \pm 2 \text{ meV}, \ j_{min} = 4; \ \diamond: E_t = 73 \pm 3 \text{ meV}, \ j_{min} = 3; \ \bigcirc: E_t = 94 \pm 5 \text{ meV}, \ j_{min} = 1.$ The gas phase rotational constant of H<sub>2</sub> is  $B \approx 7.6$  meV. From [40].

recently, Michelsen *et al.* [30,31] observed distributions that show a nonmonotonic dependence on the detected rotational state. Desorbing molecules with intermediate rotational states (*e.g.*, j = 4, 5, 6) reach the detector faster than those that do not rotate at all (j = 0) or those in higher rotational states  $(j \ge 10)$ . These experimental observations indicate a strong dependence on the molecular rotational degree of freedom. Otherwise, the rotational distributions are expected to be in thermal equilibrium with the substrate temperature at which desorption occurs. By invoking the principle of microscopic reversibility [30-34], the dissociation behavior of hydrogen on Cu can be derived from these distributions. The nonmonotonic j-dependence of the TOF peaks can be related to a nonmonotonic j-dependence of the sticking (dissociation) coefficient [35]. At low initial rotational states j, rotation inhibits sticking, while at high j, rotation promotes sticking (*cf.*, Fig. 1.2).

With recent advances in molecular beam scattering techniques, it is now even possible to determine the initial rotational state of hydrogen molecules prior to being adsorbed on metal surfaces [37-39]. Recently, Gostein and Sitz [39] directly observed, for the first time, that the sticking (dissociation) coefficient [35] of H<sub>2</sub> on Pd(111) is non-monotonically dependent on the initial rotational state of the impinging hydrogen molecule (Fig. 1.3), first decreasing with increasing initial rotational state  $(j = 0 \rightarrow 3)$ , for low j, then increasing again for higher j (j = 4, 5). This interesting feature of the sticking coefficient of H<sub>2</sub>/Pd(111) as a function of the ini-



Figure 1.4. Schematic diagram of how the molecular angular momentum **j** is spatially oriented with respect to the surface normal unit vector  $\hat{\mathbf{n}}$  for different  $A_0^{(2)}(j)$  values.  $A_0^{(2)}(j) < 0$  corresponds to a cartwheel-like rotational preference, with **j** oriented predominantly perpendicular to  $\hat{\mathbf{n}}$ .  $A_0^{(2)}(j) > 0$  corresponds to a helicopter-like rotational preference, with **j** oriented predominantly parallel to  $\hat{\mathbf{n}}$ .  $A_0^{(2)}(j) = 0$  corresponds to a spatially isotropic distribution of **j**.

tial rotational state j of the impinging H<sub>2</sub> resembles the sticking probability results inferred from rotationally state resolved time-of-flight (TOF) distribution results of Michelsen *et al.* [30] for D<sub>2</sub> associatively desorbing from Cu(111).

As for the orientational preference in associative desorption, Wetzig *et al.*, [41] using the laser-induced fluorescence (LIF) detection technique [42-44], reported the first such measurement of the preferential steric orientation for D<sub>2</sub> desorbing from Pd(100) by determining the quadrupole alignment factor  $A_0^{(2)}(j)$ . The quadrupole alignment factor  $A_0^{(2)}(j)$ , which is given by [42-45]

$$A_0^{(2)}(j) = \left\langle \frac{3j_z^2 - \mathbf{j}^2}{\mathbf{j}^2} \right\rangle_j,\tag{1.1}$$

assumes values in the range [-1,3j/(j+1)-1]. For molecules exhibiting cartwheellike motion  $(|m_j| \approx 0)$  with respect to the surface normal  $\hat{n}$ ,  $A_0^{(2)}(j) < 0$ , while those exhibiting helicopter-like motion  $(|m_j| \approx j)$  have  $A_0^{(2)}(j) > 0$ , with perfect alignment given by  $A_0^{(2)}(j) = 3j/(j+1) - 1$ , and as  $j \to \infty$ ,  $A_0^{(2)}(j) \to 2$ . A spatially isotropic distribution of the angular momentum  $\mathbf{j}$  is described by  $A_0^{(2)}(j) = 0$  (cf., Fig. 1.4). Wetzig et al. [41] observed that D<sub>2</sub> desorbing in the vibrational ground state from Pd(100) have positive alignment (indicating a preference for helicopter-like motions) which vanishes for j = 7, 8 (spatially isotropic distribution). They later observed the same qualitative features for the desorption of H<sub>2</sub> from Pd(100) [46]. Similarly, for D<sub>2</sub> desorbing in the vibrational ground state from Cu(111) Wetzig et al. [47] measured, for all final rotational states measured ( $j = 1 \to 8$ ), a small quadrupole



Figure 1.5. Results of *ab-initio* potential energy calculations (GAUSSIAN88) [57] for  $H_2/Cu$  showing (a) parallel, and (b) perpendicular orientations of the  $H_2$  relative to the Cu surface. Contour spacing is 0.4 eV and barrier height in (a) is approximately 1.6 eV. 1 AU (atomic unit)  $\approx 0.5$ Å. From [36].

alignment factor that is almost compatible with a spatially isotropic distribution  $(A_0^{(2)}(j) \approx 0)$ . Gulding *et al.* [50], using the resonance-enhanced multiphoton ionization (REMPI) detection technique [48,49], also measured a quadrupole alignment factor corresponding to a small preference for helicopter-like motion, which, in turn, increases with increasing j.

Electronic (*ab-initio*) energy calculations [36, 51–61] show that the H<sub>2</sub>/Cu potential energy (hyper-) surfaces (or PESs) possess a barrier to adsorption of about 1 eV with a substantial increase in the equilibrium H-H internuclear distance near the crest of the barrier, or the so-called *transition state* region of the potential. The existence of the activation barrier is due to the interaction between H<sub>2</sub> and the metal surface, and the interaction between the two contituent H atoms of H<sub>2</sub>. The existence of the barrier for adsorption of hydrogen on simple metals has been illustrated *via* model calculations on a jellium surface [51]. As a H<sub>2</sub> approaches a metal surface, its molecular orbitals  $(1\sigma_g \text{ and } 1\sigma_u^*)$  begin to overlap with the wavefunction of the metal *s* electrons. The H<sub>2</sub> molecular orbitals couple with the metal, producing H<sub>2</sub>metal bonding and anti-bonding states. While a bonding effect between the metal and H<sub>2</sub> can be initiated by a lowering of the  $1\sigma_g$  orbital, an increase in the metal electron kinetic energy, brought about by an orthogonalization of the metal electron wavefunctions with the H<sub>2</sub> orbitals (*via* the Pauli exclusion principle) dominates as the H<sub>2</sub> molecule first approaches the metal surface, resulting in an activation barrier. As the H<sub>2</sub> comes closer to the metal surface, the  $1\sigma_u^*$  antibonding molecular orbital broadens and its energy level lowered, becoming partially occupied at intermediate H<sub>2</sub>-metal surface distances. This partial occupation means that the H-H bond weakens and the internuclear distance increases. Meanwhile the H<sub>2</sub>-metal bonding continues to increase. Finally, the H<sub>2</sub> internuclear bond breaks and the individual H atoms are free to bond with the metal surface. Once past the activation barrier that might exist, a H must bond to the surface. Hydrogen interacts with a metal surface in much the same way that H<sub>2</sub> does. However, because a H has a half filled orbital, it can accommodate an extra electron from the metal. The energy gain from the coupling of the H 1*s*-metal *sp* electrons results in a hydrogen bonding level typically 6-10 eV below the Fermi level, and explains all the measured chemisorption energy for H on the simple metals [62].

Results of dissociation dynamics calculations [33, 34, 63–67], consistent with the idea of molecular bond-length stretching in the transition state, suggest that the vibrational energy can help an incident molecule overcome the barrier to dissociation. On the other hand, quasi-classical and quantum mechanical calculations [33, 68–74], most of them multi-dimensional, done to explain the role of rotational excitation on surface reactions have varying conclusions. Some calculations show a sticking probability that is—increasing with the initial rotational state j [68, 70], independent of j [71], decreasing with j [33, 69, 72] and, recently, nonmonotonically dependent on the initial rotational state j [73, 74]. Ab-initio calculations of the PES for H<sub>2</sub> dissociating on Cu surfaces [57–61] also show a strong dependence on the molecular orientation (*cf., e.g.,* ab-initio PES calculation results of [57] shown in Fig. 1.5), and significant corrugations within the unit cell [36, 57–61]. This strong corrugation, most believe (*e.g.,* [41, 47, 50, 73, 75–78]), is necessary in multi-dimensional calculations to understand and describe the trends found experimentally for the variation of the sticking probability of H<sub>2</sub> on copper surfaces.

Of the several factors that influence the dynamics of hydrogen-solid surface reactions (e.g., relative coordinates of the reaction partners (hydrogen molecule and solid surface), molecular internal degrees of freedom, surface degrees of freedom (surface phonons and electron-hole pairs), influence of surface defects and steps), one of the more important factors is MOLECULAR ORIENTATION. Molecules, in general, would be adsorbed on surfaces with preferential orientations, and we expect that such orientation preferences would ultimately determine how the molecule responds to the orientation dependence of the interaction potential energy surface describing the reaction. This thesis is based, in part, on earlier and ongoing studies [36,40,82–90] on orientational effects on the activated [36,82–87] and the non-activated [40] dissociation of hydrogen molecules on metal surfaces, and the reverse process of association and then desorption from metal surfaces [83–90]. In the following chapter, Chapter 2, we give a full description of the model we adopted to study the dynamics of hydrogen on copper and palladium surfaces. We did quantum mechanical model calculations using the coupled-channel method [33,64] and the concept of a local reflection matrix [79]. Our model potential is based on qualitative features of available PES plots for the  $H_2/Cu$  surface [36, 57–61] (e.g., ab-initio PES calculation results of [57] shown in Fig. 1.5) and  $H_2/Pd$  surface [91,92] systems. We took advantage

of the convenience gained in using the concept of a reaction path (cf., e.g., [64]). In Chapter 3, we give a discussion of our results concerning the rotational effects on the dissociative adsorption dynamics and inelastic scattering dynamics of hydrogen on a copper surface. In Chapter 4, we give a discussion of the corresponding rotational effects on the dynamics of the reverse process of associative desorption, where H(D)atoms initially adsorbed on the surface come together and desorb as  $H_2(D_2)$  from the surface. Our theoretical studies on the influence of molecular orientation on the dynamics of  $H_2(D_2)$  reactions with metal surfaces, viz., Cu(111) and Pd(111), which are examples of an activated and a non-activated system, respectively, show very interesting, surprising and general results. We will show that due to the inherent orientational dependence of hydrogen-solid surface reactions and the coupling between the different degrees of freedom involved, two factors, viz., Steering or the DYNAMICAL REORIENTATION factor and Rotational-Translational Energy Transfer or the ROTATIONAL ASSISTANCE via BOND-LENGTH EXTENSION factor, come into effect [36]. Furthermore, we will show that the Steering Effect, which is due to the anisotropic nature of the PES, dominates over the Energy Transfer Effect for low initial rotational states j. For high j, the Energy Transfer Effect, which arises from the strong coupling between the rotational motion and the motion along the reaction path, dominates. As a result of the competition between these two processes/factors, the dissociation probability of  $H_2(D_2)$  on Cu(111), a paradigm of an activated system, for example, would show a nonmonotonic dependence on the initial rotational state of the impinging  $H_2(D_2)$ , as observed experimentally. We will also show that the efficacies of these two factors are strongly dependent on the incidence translational energy of the impinging hydrogen molecule [85]. This prediction was later observed for the  $H_2/Pd(111)$  system [39], an example of a non-activated system, which we will discuss in detail in Chapter 5. We will show that we were able to consistently relate the calculated adsorption results with that of the desorption results [85] and, for the first time, reproduce the experimentally observed initial cooling, then a mild heating, followed by a cooling again of the rotational temperature of the desorbing hydrogen molecules with respect to the surface temperature. Upon considering the reverse process of associative desorption, we will show that due to the inherent orientational dependence of the hydrogen-solid surface reaction, another factor takes effect, viz., Dynamical Quantum Filtering [88-90]. And by taking advantage of the inherent nature of the desorption process to be orientation dependent, we suggested that it might actually be possible to produce oriented  $H_2(D_2)$ , which was up to now impossible. The process involves permeating H(D)atoms through the bulk of, e.g., a copper single crystal and using the Cu(111) surface as a dynamical quantum filter. Due to Dynamical Quantum Filtering, fast desorbing molecules would exhibit helicopter-like rotational preference and slow desorbing molecules would exhibit cartwheel-like rotational preference. By applying energy-resolved detection techniques [88–90], we could then select from among the desorbing molecules for helicopter-like rotating molecules or cartwheel-like rotating molecules. We will also explain the experimentally observed suprisingly low rotational alignment [41, 46, 47, 50]. In Chapter 5, we will show that the experimental observations for the dissociative adsorption and associative desorption dynamics of  $H_2$  on Pd(111) could also be explained by considering the three factors mentioned above, indicating that Steering, Energy Transfer via Bond-Length Extension, and

Dynamical Quantum Filtering are general, dynamical features of orientation dependent reactions [40]. In Chapter 6, we give our overall conclusions and a summary of our work.

# Chapter 2 The Model System

As mentioned in the previous chapter, one of the most exciting challenges of presentday surface science is, undoubtedly, the task of developing a detailed microscopic picture of dynamical processes occurring on solid surfaces. To this purpose, many systems have drawn considerable interest and studies, one of these being the hydrogen on metal system, which has become one of the benchmark systems, particularly on the nature of the dissociative adsorption process, and the reverse process of association and then desorption (cf., [23] and references found therein). The dynamics of such interactions between a molecule and a surface is dependent on the relative coordinates of the reaction partners (molecule and surface) and the internal degrees of freedom of the molecule. To this list of variables we must add the surface degrees of freedom (e.g., surface phonons and electron-hole pairs), and recognize the possible influence of surface defects and steps. It is no doubt a formidable task to obtain a full theoretical description which includes all degrees of freedom. A way around this would be for us to choose model systems for which the influence of certain degrees of freedom is minimized. Alternatively, we could choose to systematically investigate only those degrees of freedom on which we can exert considerable control. However, since the positions and velocities of the nuclei and the electronic state of the system change throughout the interaction of a molecule with a surface, it is not possible to follow the ongoing events continuously. At best, we can only hope to infer the detailed dynamics from a series of information regarding the system, before, during, and after the interaction.

Many of the dynamical processes (e.g., dissociative adsorption and associative desorption) occurring in nature are believed to be essentially electronically adiabatic (cf., e.g., [93]) and governed by a single Born-Oppenheimer potential energy (hyper-) surface (PES). Because of the smaller mass of the electrons, they may be considered capable of immediately reacting to the motion of the nuclei, relaxing virtually instantaneously, such that the force on the nuclei is that characteristic of the ground-state of the electron system. It is this electronic ground-state which will then contribute to the interaction potential of the interacting nuclei, serving as the potential energy function for the nuclear motion.

In studying the interaction of a gas-phase molecule with a solid surface, it is, thus, standard theoretical practice to adopt the Born-Oppenheimer approximation, and formulate the problem in terms of the motion of some representative point or points over a PES. Then the problem of studying the interaction of a molecule with a surface reduces to—(1) obtaining the relevant PES, and (2) solving the



Figure 2.1. The model system showing a diatomic molecule (molecular orientation with respect to the surface normal given by  $\theta$ , surface to center-of-mass (CM) distance  $Z_{CM}$ , and bond-length r) approaching a flat surface perpendicularly.  $m_A$  and  $m_B$  correspond to the masses of the constituent atoms of the diatomic molecule. Note that there is no azimuthal dependence because normal energy scaling (a flat surface) was assumed. From [36].

corresponding equations of motion. From the above reasoning it is obvious that, in order to make progress in understanding the dissociative adsorption and associative desorption of hydrogen molecules on or from metal surfaces, we require a good PES for the molecule-surface interaction.

Following the practice mentioned above, we did dynamical calculations, using the model system shown in Figs. 2.1 & 2.6 (inset) for a *rigid surface* and a *dynamic surface*, respectively.

### 2.1 Rigid Surface

For a rigid surface, we considered the model system shown in Fig. 2.1, and studied the effect of rotation on the dissociative adsorption (associative desorption) process. Because normal energy scaling is observed for Cu(111) (cf., e.g., [31,105]), we only considered the reaction of a hydrogen molecule—with a center-of-mass distance Z above the equilibrium position of the surface oscillator, an internuclear distance or bond-length r, and a molecular axis orientation  $\theta$  with respect to the surface normal—incident perpendicular to a flat metal surface.



Figure 2.2. Comparison of transmission coefficient T vs. incidence energy  $E_t$  curves for a wide ( $\alpha = 1.0 \text{ Å}^{-1}$ ) and a narrow ( $\alpha = 6.0 \text{ Å}^{-1}$ ) cosh<sup>2</sup>(x)-type potential. Activation energy was taken to be  $E_a = 0.536$  eV. From [36].

#### 2.1.1 The 1-Dimensional Activation Barrier

From earlier experiments (cf., e.g., [10, 11, 20, 24, 28, 30-32] and references found therein), using seeded molecular-beam scattering and state-resolved time-of-flight (TOF) measurements of desorption, done to study the detailed dependence of the dissociation probability on the translational, vibrational, and rotational degrees of freedom, and on the surface temperature, we now know that the dissociation of hydrogen on the low index surfaces of Cu is hindered by a considerable energy barrier. This suggests that we could think of the dissociation of hydrogen on the low index surfaces of Cu as a 1-D scattering problem, with a potential barrier of the form—

$$V(s) = \frac{E_a}{\cosh^2(\alpha s)},\tag{2.1}$$

where  $E_a$  is the activation barrier/potential barrier height ( $E_a = 0.536$  eV, this is based on parameters used by previous dynamical calculations) [33,64],  $\alpha$  is the width parameter and s is the reaction coordinate. Analytical solution [81] of the corresponding Schrödinger equation gives a functional form for the transmission coefficient T, which corresponds to the sticking/adsorption probability in the gas-surface interaction problem. The dependence of T on the incidence energy,  $E_t$ , is shown in Fig. 2.2. The "S"-shaped sticking probability vs. energy curve results, obtained by previous dynamical calculations (e.g., [33,66,67,71,73]) and experiments (e.g., [10]) done to study the associative desorption/dissociative adsorption process of H<sub>2</sub>/Cu systems, are qualitatively reproduced here. Note that the plot can be divided into



Figure 2.3. Results of *ab-initio* potential energy calculation (GAUSSIAN88) [57] for  $H_2/Cu$  showing (a) parallel, and (b) perpendicular orientations of the  $H_2$  molecule relative to the Cu surface. Contour spacing is 0.4 eV and barrier height in (a) is approximately 1.6 eV. The dashed line connecting the potential minimum in (a) represents the reaction path. 1 AU (atomic unit)  $\approx 0.5$ Å. From [36].

two regions—(1)  $E_t < E_a$  where the mechanism for transmission is through tunneling, and (2)  $E_t > E_a$  where the mechanism for transmission is through the utilization of the available translational/kinetic energy to overcome the barrier. Another point that can be observed is that the width of the potential barrier (manipulated through the parameter  $\alpha$ ) determines the width of the transition region where the sticking probability value changes from 0 to 1.

#### 2.1.2 The Orientationally Anisotropic Potential Barrier and the Effective Molecular Bond-Length for a Rigid Surface

Electron energy calculations [51-56, 58, 59, 61], as well as experiments (e.g., [26]), also show that the form of relevant PESs is strongly dependent on the orientation of the hydrogen molecular axis with respect to the metal surface. We again show a typical example of this dependence in Fig. 2.3 for the case when the molecular axis is artificially kept parallel ( $\theta = \pi/2$ , Fig. 2.3(a)), and when the molecular axis is artificially kept perpendicular ( $\theta = 0$ , Fig. 2.3(b)) to the surface. Two things are immediately evident. First, there is a "well" after the potential barrier for the

16





Figure 2.4. A molecular orientation dependent activation barrier  $V(s, \theta)$  ( $E_a = 0.536 \text{ eV}$ ,  $V_1 = 1.0 \text{ eV}$ ,  $\beta = 0.25$ , and in this figure  $\alpha = 1.0 \text{ Å}^{-1}$ ). The +s-region corresponds to the surface side. The upper figure shows how the activation barrier changes with the molecular orientation. From [36].

 $\theta = \pi/2$  orientation, whereas, no such "well" exists for the  $\theta = 0$  orientation. This means that, most likely, a molecule with a  $\theta = 0$  orientation will not be adsorbed. Second, there is a distinct difference in the curvature of the reaction path (indicated by the dashed line in Fig. 2.3(a)) for the two orientations. Assuming that the curvature of the reaction path changes as the molecular orientation changes from  $\theta = 0$  to  $\theta = \pi/2$ , then an appropriate molecular orientation dependent potential barrier is (cf., Fig. 2.4) [36]—

$$V(s,\theta) = \frac{E_a}{\cosh^2(\alpha s)} (1 - \beta \cos^2 \theta) + V_1 \cos^2 \theta \frac{[1 + \tanh(\alpha s)]}{2}$$
(2.2)

where  $\beta$  is an additional parameter that determines the degree of anisotropy of the activation barrier.

We show a typical potential in Fig. 2.4. For a molecule incident with an orientation parallel to the surface  $\theta = \pi/2$ , it encounters a  $\cosh^2(s)$ -type potential. On the other hand, a molecule with an orientation perpendicular to the surface  $\theta = 0$  will encounter a rather smooth step potential with a finite, non-zero peak after the transition region. Thus, a molecule with a parallel orientation relative to the surface will most likely be adsorbed onto the surface as compared to a molecule with a perpendicular orientation relative to the surface.

Going back to Fig. 2.3, it is obvious from the PES plots that each point along the reaction path (corresponding to a particular value of s or Z) corresponds to a particular molecular bond-length r. Thus, we have r(s) or r(Z). We can immediately see that the bond-length r increases exponentially with s. Also, at distances Zsufficiently far from the surface (corresponding to a range of values of s from  $s = -\infty$ ), r takes the value  $r_0$ , the gas phase equilibrium internuclear distance. Upon reaching some distance relative to the surface Z, r begins to increase rapidly with s. We assumed that the bond-length has the following s-dependence—

$$r(s) = r_0 \sqrt{[1 - \exp(\alpha s)]}.$$
 (2.3)

#### 2.1.3 The Model Hamiltonian for a Rigid Surface

The Hamiltonian for the model system corresponding to a rigid surface described above (cf., Fig. 2.1) has the form—

$$H(Z, r, \theta) = -\frac{\hbar^2}{2\mu} \partial_r^2 - \frac{\hbar^2}{2M} \partial_Z^2 + \frac{\hbar^2}{2\mu r^2} L^2 + V(Z, r, \theta), \qquad (2.4)$$

where

$$M = m_D + m_D = 2m_D, (2.5)$$

$$\mu = \frac{m_D m_D}{m_D + m_D} = \frac{1}{2} m_D, \qquad (2.6)$$

$$L^{2} = -\left[\frac{1}{\sin\theta}\partial_{\theta}(\sin\theta\partial_{\theta}) + \frac{1}{\sin^{2}\theta}\partial_{\phi}^{2}\right], \qquad (2.7)$$

and  $V(Z, r, \theta)$  is the relevant PES, which in this case is the ground state energy of the electron system. We took advantage of the convenience gained in using a new coordinate system in terms of  $(s, \rho, \theta)$  (cf., Fig. 2.5), derivable from the concept of a reaction path or path of least potential [57,63,64,80,93-97], which is based on contour plots of available PESs (e.g., Fig. 2.3). The variable s stands for the reaction path coordinate along the least potential on the PES. Far from the surface it corresponds to the Z coordinate. The reference point is the position where the peak of the acivation barrier is, and far from the surface s takes on negative values. The variable  $\rho$  is the reaction vibration coordinate orthogonal to s at every point on s. The polar angle  $\theta$  gives the molecular axis orientation with respect to the surface normal. This coordinate is normal to the plane defined by s and  $\rho$ . (For more



Figure 2.5. A typical reaction path curve  $C_0$ , which corresponds to the dashed line in Fig. 2.3(a). With this curve  $C_0$ , we can derive for the relation between the coordinates  $(Z, \tau)$  and  $(s, \rho)$ . Far from the surface, the reaction path coordinate s, along  $C_0$ , corresponds to the center-of-mass coordinate Z. Near the surface, s corresponds to the intra-molecular distance r. The  $\rho$ -coordinate is always perpendicular to s, as r is perpendicular to Z.

discussion regarding the change in coordinate system, cf., e.g., [63, 64, 93-97].) Due to the difference in time scales of molecular vibration and rotation, it is possible to decouple molecular vibration from rotation, as a first approximation [80]. The model Hamiltonian, after transformation using a mass-weighted reaction path coordinate

s, will have the form—

$$H(s,\rho,\theta) = -\frac{\hbar^2}{2\mu}\partial_{\rho}^2 - \frac{\hbar^2}{2\mu}(\frac{r_0}{\rho - r_0})^2\partial_s^2 + \frac{\hbar^2}{2I(s)}L^2 + V(s,\rho,\theta)$$
(2.8)

where  $r_0$  is the radius of curvature of the reaction path at the curved region (cf., [64] for a detailed derivation). If we restrict the system to its vibrational ground state and convert back to non-mass-weighted coordinates, the model Hamitonian takes the final form—

$$H(s,\theta) = -\frac{\hbar^2}{2M}\partial_s^2 + \frac{\hbar^2}{2I(s)}L^2 + V(s,\theta),$$
(2.9)

where

$$I(s) = \mu r^2(s), (2.10)$$

and  $V(s,\theta)$  is the potential barrier that the representative point of the system encounters on its way along the reaciton path. The form of the *s*-dependence of the internuclear distance *r* is discussed in the following sub-section. Numerical calculations were done with the coupled-channel method [33,64] and using the concept of a local reflection matrix [79].

#### 2.2 Dynamic Surface

For a dynamic (non-rigid) surface, we considered the model system shown in Fig. 2.6 (inset) and studied the effect of rotation on the dissociative adsorption process, as well as how the adsorption probability curve will change when a dynamic surface is considered. As mentioned earlier (§2.1), because normal energy scaling is observed for Cu(111) (cf., e.g., [31,105]), we only considered the reaction of a hydrogen molecule—with a center-of-mass distance Z above the equilibrium position of the surface oscillator, an internuclear distance or bond-length r, and a molecular axis orientation  $\theta$  with respect to the surface normal-incident perpendicular to a flat metal surface. The motion of the surface lattice is represented by an array/set of locally uncoupled Einstein oscillators, each having a mass  $M_S$  ( $\approx 63$  dalton, mass of one Cu atom), and an oscillator frequency  $\omega_S$  given by the surface Debye temperature of copper ( $\theta_D \approx 315$  K, roughly equivalent to the top of the surface phonon band). This Einstein approximation has been used extensively in surface scattering [64, 108–110], and is valid provided the collision energies and energy transfers involved are large compared to the phonon band width. Furthermore, due to the relatively small size of our impinging molecule (hydrogen) compared to each individual surface atom, most scattering processes occur between an impinging molecule and a single surface atom, further justifying our choice of adopting the Einstein approximation.

#### 2.2.1 The Orientationally Anisotropic Potential Barrier and the Effective Molecular Bond-Length for a Dynamic Surface

We treat the coupling between the rotational degree of freedom of the impinging molecule and the vibrational degree of freedom of the surface lattice (modeled as



Figure 2.6. A typical reaction path curve,  $C_0$ , which corresponds to the dashed line in Fig. 2.3(a) and the curve shown in Fig. 2.5, relative to the coordinates (Z, r). Far from the surface, the reaction path coordinate along  $C_0$ corresponds to the center-of-mass coordinate Z. Near the surface, s corresponds to the intra-molecular distance r.  $\Delta x$  gives the relative shift of the whole reaction path curve  $C_0$  upwards  $(C_+)$ , or downwards  $(C_-)$ , as the surface atom vibrates about its equilibrium position,  $x_0$ . (Inset) The model system showing a diatomic molecule (molecular orientation with respect to the surface normal given by  $\theta$ , center-of-mass (CM) to surface oscillator distance  $Z_{CM}$ , and bond-length r) approaching a flat surface perpendicularly.  $m_D$  corresponds to the mass of the constituent atoms of the impinging diatomic molecule (hydrogen). Note that there is no azimuthal dependence because normal energy scaling (a flat surface) was assumed. x gives the position of the surface oscillator of mass  $M_S$  relative to some fixed reference. From [82].

independent Einstein oscillators) by attaching the orientationally anisotropic PES of [36] rigidly, via the center-of-mass coordinate Z, to the Einstein oscillators (taken as harmonic oscillators) [103, 104, 108–112]. Then the PES has the form—

$$V(Z, r, \theta, x) = V(Z - x, r, \theta) + \frac{1}{2}M_S\omega_S^2 x^2,$$
(2.11)

where  $V(Z, r, \theta)$  is the relevant PES seen by the representative point of the system for a particular orientation  $\theta$  of the impinging molecule relative to the normal to the rigid surface. r is the internuclear distance or bond-length of the impinging molecule. x gives the position of the surface oscillator relative to some fixed reference (*cf.*, inset, Fig. 2.6). (The difference between results obtained using a rigid surface and a dynamic surface is then due only to the dynamics and not to changes in the barrier height or shape when the oscillator is excited.)

Again, we adopted, for convenience, a new coordinate system in terms of  $(s, \rho, \theta)$ , as described in §2.1.3. The variable s stands for the reaction path coordinate along the path of least potential on the PES. Far from the surface it corresponds to the Z-coordinate. The reference point is the position where the peak of the activation barrier is, and far from the surface, s takes on negative values. In Fig. 2.6, we show a typical reaction path curve for a given orientation of the impinging molecule, say parallel to the surface (curve  $C_0$ , rigid surface). The variable  $\rho$  is the reaction vibration coordinate orthogonal to s at every point along curve  $C_0$ . The polar angle,  $\theta$ , still gives the molecular axis orientation with respect to the surface normal. This coordinate is normal to the plane defined by s and  $\rho$ .

If we restrict the surface oscillator (surface atom) to move up and down normal to its equilibrium position (as described above), then the corresponding reaction paths of the resulting PES will move up and down (curves  $C_+$  and  $C_-$ , respectively, in Fig. 2.6) normal to the equilibrium position of the reaction path of the PES for a rigid surface (curve  $C_0$  in Fig. 2.6). (Because we assumed a flat surface, vibrations along the surface plane do not influence the reaction.) We can immediately see that the projections of the positions of the activation barrier peaks of curves  $C_+$  and  $C_$ along curve  $C_0$  do not land on the same point along  $C_0$ . If the variation ( $\Delta x$ ) in the position of the surface atoms relative to its equilibrium position  $(x_0)$  is small enough, the coupling Eq. (2.11) results in a virtual motion of the activation barrier along the reaction path described by  $C_0$  without a change in barrier height. We can then make the approximate transformation—

$$(Z - x, r, \theta) \Rightarrow (s - x, \rho - x, \theta).$$
 (2.12)

In carrying out the coupling described in Eq. (2.11), we considered the orientationally anisotropic model PES for a rigid surface, expressed in terms of s and  $\theta$ , given in [36]. Using the approximate transformation Eq. (2.12), we have the final potential given by—

$$V(s-x,\theta) = \frac{E_a}{\cosh^2[\alpha(s-x)]} (1-\beta\cos^2\theta) +V_1\cos^2\theta \frac{\{1+\tanh[\alpha(s-x)]\}}{2}, \qquad (2.13)$$

where  $\alpha$  is the width parameter [36]. In addition, for a rigid surface, we know that each point along the reaction path (of the PES) corresponds to a particular value of r (the bond-length). Thus, we have r(s). Following the arguments proposed in [36,74], we assumed that, upon applying the approximate transformation Eq. (2.12), the bond-length has the following s-dependence-

$$r(s-x) = r_0 \sqrt{1 - \exp[\alpha(s-x)]},$$
 (2.14)

where  $r_0$  is the gas phase equilibrium internuclear distance.

#### 2.2.2 The Model Hamiltonian for a Dynamic Surface

The Hamiltonian for the model system described above has the form-

$$H(Z, r, \theta, x) = -\frac{\hbar^2}{2\mu} \partial_r^2 - \frac{\hbar^2}{2M} \partial_Z^2 + \frac{\hbar^2}{2\mu r^2} L^2 + V(Z - x, r, \theta) -\frac{\hbar^2}{2M_S} \partial_x^2 + \frac{1}{2} M_S \omega_S^2 x^2, \qquad (2.15)$$

where,

$$M = m_D + m_D = 2m_D, (2.16)$$

$$\mu = \frac{m_D m_D}{m_D + m_D} = \frac{1}{2} m_D, \qquad (2.17)$$

$$L^{2} = -\left[\frac{1}{\sin\theta}\partial_{\theta}(\sin\theta\partial_{\theta}) + \frac{1}{\sin^{2}\theta}\partial_{\phi}^{2}\right], \qquad (2.18)$$

and  $V(Z, r, \theta)$  is the relevant PES (as mentioned in §2.2.1), which in this case is the ground state energy of the electron system. The last two terms of the model Hamiltonian (Eq. (2.15)) correspond to the Hamiltonian of the surface oscillator with mass  $M_S$  and frequency  $\omega_S$ . Due to the difference in the time scales of molecular vibration and molecular rotation, as well as, molecular vibration and surface vibration, it is possible to decouple molecular vibration from the other two degrees of freedom, as a first approximation. After doing the approximate transformation to the reaction path coordinate (Eq. (2.12)), and then restricting the system to its molecular-vibrational ground state, we get the following intermediate model Hamiltonian—

$$H(s,\theta,x) = -\frac{\hbar^2}{2M}\partial_s^2 + \frac{\hbar^2}{2I(s-x)}L^2 + V(s-x,\theta) - \frac{\hbar^2}{2M_S}\partial_x^2 + \frac{1}{2}M_S\omega_S^2x^2, \quad (2.19)$$

where the moment of inertia is given by-

$$I(s-x) = \mu r^2(s-x),$$
(2.20)

 $V(s-x,\theta)$  is the PES expressed in terms of reaction path coordinates (Eq. (2.13)), and r is the *s*-dependent bond-length (Eq. (2.14)). Since we restricted the system to be in its molecular-vibrational ground state, the extra terms due to the approximate transformation (Eq. (2.12)) are reduced to mere constants which we can accommodate into the potential term  $V(s-x,\theta)$ . We then define a new set of dimensionless variables (S, X)—

$$S = \alpha s, \tag{2.21}$$

$$X = \gamma^{-1} \alpha x, \tag{2.22}$$

where the coupling constant  $\gamma$  is defined as—

$$\gamma^{-1} = \sqrt{\frac{M_S \omega_S}{\hbar \alpha^2}}.$$
(2.23)

The final dimensionless Hamiltonian is then given by-

$$H(S,\theta,X) = -\frac{\hbar^2 \alpha^2}{2\mu} \partial_S^2 + \frac{\hbar^2}{2I(S-\gamma X)} L^2 + V(S-\gamma X,\theta) + \hbar \omega_S (-\frac{1}{2} \partial_X^2 + -\frac{1}{2} X^2), \qquad (2.24)$$

where the relevant PES takes the final form-

$$V(S - \gamma X, \theta) = \frac{E_a}{\cosh^2[\alpha(S - \gamma X)]} (1 - \beta \cos^2 \theta) + V_1 \cos^2 \theta \frac{\{1 + \tanh[\alpha(S - \gamma X)]\}}{2}, \qquad (2.25)$$

and the moment of inertia is given as-

$$I(S - \gamma X) = \mu r^2 (S - \gamma X) = \mu r_0^2 [1 + \exp(S - \gamma X)].$$
 (2.26)

## Chapter 3

# Rotational Effects in the Dissociative Adsorption and Inelastic Scattering Dynamics of $D_2/Cu(111)$

### 3.1 Rigid Surface

#### 3.1.1 Steering & Energy Transfer Effects

In Fig. 3.1 we see that the general effect of putting part of the available energy of the incident molecule [98] into its rotational degree of freedom is to decrease the corresponding sticking probability  $S_0$  (sticking probability for initial rotational state j = 0). This came about as a result of the anisotropic PES reorienting (rotating) the molecule, steering it to different regions of the PES. Thus, there is a decrease in the amount of available energy to overcome the barrier to dissociation. This reorientation of the molecule by the anisotropic potential is called *Steering Effect*. The prominent "S"-shape of the  $S_0$  vs.  $E_t$  curve, characteristic of activated systems, qualitatively agrees with initial results of Kasai and Okiji [33] for low incidence translational energies. There was a general increase in  $S_0$  as a function of  $E_t$ .

The particular form of the potential  $V(s, \theta)$  results in a selection rule where molecules in even (odd) initial rotational states end up in even (odd) final rotational states, *i.e.*, even (odd) rotational states are coupled only to even (odd) rotational states. In Fig. 3.2 we show a comparison between the reflection probabilities  $R_{j0}$  of a molecule, initially in the rotational state j = 0, with different incidence energies and barrier widths encountered. In general, for a given width of the activation barrier (determined by fixing the value of  $\alpha$  in Eqs. (2.1) & (2.2)), molecules prepared with higher incidence translational energies exhibited higher probabilities of rotational excitations (final j states reaching higher values). This implies that, on its way towards the surface, the high sensitivity of the molecule to the anisotropy of the potential causes it to reorient (rotate) out of its initially prepared orientation, seeking the *path of least resistance* (*path with the least potential*, corresponding to the best orientation for adsorption). For a given incidence energy, molecules encountering a wider barrier (smaller  $\alpha$ ) will exhibit higher probabilities of rotational excita-



Figure 3.1. Comparison of the corresponding  $S_0$  vs.  $E_t$  curves for a homonuclear diatomic molecule encountering a  $\cosh^2(x)$ -type activation/potential barrier with different widths (given by  $\alpha = 2.5 \text{ Å}^{-1}$  and  $\alpha = 5.0 \text{ Å}^{-1}$ ) for the case when the rotational degree of freedom is not considered ( $\diamond$ ), and when it is considered (filled  $\diamond$ ). Activation energy was taken to be  $E_a = 0.536$  eV. From [36].

tions. This in turn implies that a wider potential is more effective in reorienting the molecule.

In Fig. 3.3(a), we show how the  $S_0$  vs.  $E_t$  curve depends on the initial rotational state j of impinging molecule, suppressing the Steering Effect ( $\beta = 0.0$ ,  $V_1 = 0$  eV, no potential anisotropy) in the PES (cf., Eq. (2.2)). Only the *R*-T Energy Transfer Effect (*i.e.*, Rotational to Translational Energy Transfer) is present through the coupling of the rotational motion with the motion along the reaction path. There is



Figure 3.2. Comparison of the corresponding  $R_{j0}$  vs. j curves (a)-(b) for a molecule encountering a potential barrier with a fixed barrier width, and with different incidence energies; (c)-(d) for a molecule encountering a potential barrier with different barrier widths (determined by  $\alpha$  [Å<sup>-1</sup>] and a fixed incidence energy  $E_t$ . Activation energy was taken to be  $E_a = 0.536$  eV. From [36].

a pronounced enhancement of the dissociative adsorption probability as the initial rotational state j increases (shown by the leftward shift of the "S"-shaped curve for increasing j).

In Fig. 3.3(b), we show the effect of turning on the Steering Effect ( $\beta \neq 0.0$ ,  $V_1 \neq 0.0$ , with potential anisotropy) in the PES (cf., Eq. (2.2)). We can clearly see



Figure 3.3. Initial rotational state *j*-dependent adsorption probabilities for a homonuclear diatomic molecule in the vibrational ground state encountering (a) an orientationally isotropic potential barrier ( $\beta = 0.0$ ,  $V_1 = 0.0$  eV), and (b) an orientationally anisotropic potential barrier ( $\beta = 0.25$ ,  $V_1 = 1.0$  eV). Width of the potential barrier (determined by  $\alpha = 4.5$  Å<sup>-1</sup>) is the same for the two cases. Activation energy was taken to be  $E_a = 0.536$  eV. The homomuclear diatomic molecule was assumed to be D<sub>2</sub>, with a gas phase rotational constant  $B \approx 3.8$  meV. From [36].

that the enhancement of the adsorption probability as the initial rotational state j increases seen before is considerably decreased.

To get a clearer view of what the Steering Effect does, we show in Fig. 3.4(a) the m-resolved initial rotational state dependence of the dissociative adsorption probability for a constant translational energy of 0.6 eV. If we interpret m as one of the 2j + 1 possible Z-components of the total angular momentum **j**, then each



Figure 3.4. Sticking coefficient  $S_j$  for a homonuclear diatomic molecule as a function of its initial rotational state j. (a) *m*-resolved (b) summed over all m ( $\alpha = 4.5 \text{ Å}^{-1}$ ,  $\beta = 0.25$ ,  $E_a = 0.536 \text{ eV}$ ,  $V_1 = 1.0 \text{ eV}$ ,  $E_t = 0.60 \text{ eV}$ ). The homonuclear diatomic molecule was assumed to be  $D_2$ , with a gas phase rotational constant  $B \approx 3.8 \text{ meV}$ . From [36].

m represents one particular orientation of the molecule.  $m \approx 0$  corresponds to molecules doing cartwheel-like rotations, *i.e.*, molecular orientation is predominantly perpendicular to the surface, and  $m \approx j$  corresponds to molecules doing helicopterlike rotations, *i.e.*, molecular orientation is predominantly parallel to the surface. Consider one particular initial rotational state, say j = 1, in Fig. 3.4(a). Note the big difference in the corresponding sticking probability for |m| = 0 (perpendicular orientation) and |m| = j = 1 (parallel orientation). This Steering Effect would, however, be dominated by the *R*-*T* Energy Transfer Effect at initial rotational states that are high enough. In this region (region of high initial rotational states), the sticking probability for different *m* values (different orientations) would almost be the same. With high initial rotational states the surface cannot distinguish one orientation from the other, and rotational energy is large enough to contribute to the translational energy, helping the molecule overcome the activation barrier.

In Fig. 3.4(b), we show the combined effect on the total sticking probability. We can see that there is a very slight initial decrease in the sticking probability (*cf.*, value of  $S_j$  for j = 0 and j = 1) and then a gradual increase in the sticking probability for j > 1.

Increasing the potential barrier range/width (through the parameter  $\alpha$ ) changes the sticking probability curve (*cf.*, Figs. 3.4 & 3.5). This change is particularly noticeable at the low initial rotational state region ( $j \leq 8$ ), where a wider potential allows more time for an initially unfavorably oriented molecule to reorient to a more favorable one. Thus, the corresponding sticking probability increases. On the other hand, there is a corresponding decrease in the sticking probability for an initially favorably oriented molecule. The total effect is an initial decrease, and then a final increase in the sticking probability (*cf.*, Fig. 3.5(b)).

Comparing Figs. 1.2 & 3.5(b), we see that we were able to reproduce the experimental observation of an initial decrease and then a final increase of the sticking probability as a function of the initial rotational state j of D<sub>2</sub> at a particular incidence translational energy  $E_t = 0.60$  eV. In order to compare Figs. 1.2 & 3.5(b), we can draw an imaginary vertical line parallel to the ordinate and intersecting the abscissa of Fig. 1.2 at 0.6 eV. This imaginary vertical line would then intersect the "S"-shaped curves corresponding to j = 0.5, 10, 14 approximately at relative adsorption probability values of—0.43, 0.25, 0.50, 0.89, respectively.

Furthermore, if we imagine that the spaces between the curves corresponding to j = 0 and j = 5 are filled by curves corresponding to j = 1, 2, 3, 4, 5, going from left to right. Then the imaginary line intersects all points of each curve at the sticking probability corresponding to an incidence energy of 0.6 eV. Proper choice of the parameters for the potential width  $(\alpha)$ , the anisotropy  $(\beta)$ , and the barrier heights  $(V_0 \text{ and } V_1)$  will give a more quantitative reproduction of experimental observations.

Based on physical arguments, our previous study [36], and earlier studies on the subject (e.g., [10, 30, 73, 74] and references found therein) there are two competing factors working for the dissociative adsorption process, viz.,-

- 1. Steering or the DYNAMICAL REORIENTATION Factor, and
- 2. Rotational-Translational Energy Transfer or the ROTATIONAL ASSIS-TANCE via BOND-LENGTH EXTENSION Factor

Steering Effect pertains to reorientation of the molecule in an attempt to follow the path of least resistance, *i.e.*, to assume an orientation with the least potential, which is due to the strong molecular orientation dependence of the PES. We could also say that this pertains to the capability of the orientation-sensitive potential energy surface to reorient the molecule from an initially unfavorable orientation (*i.e.*, perpendicular to the surface) to a favorable orientation (*i.e.*, parallel to the surface



Figure 3.5. Sticking coefficient  $S_j$  of a D<sub>2</sub> impinging a Cu(111) as a function of its initial rotational state j. (a) m-resolved (b) summed over all m ( $\alpha = 1.5 \text{ Å}^{-1}$ ,  $\beta = 0.25$ ,  $E_a = 0.536 \text{ eV}$ ,  $V_1 = 1.0 \text{ eV}$ ,  $E_t = 0.60 \text{ eV}$ ). The gas phase rotational constant of D<sub>2</sub> is  $B \approx 3.8 \text{ meV}$ . From [36].

(cf., Fig. 3.6), or vice-versa. The orientation of the molecule upon encountering the surface determines the ground state energy of the  $D_2/Cu(111)$  electron system, which, in turn, serves as the effective/relevant PES that determines the dynamics of the molecule-surface reaction. From the results of *ab-initio* calculations in Fig. 2.3, we can see that there is a big difference in the PES plot for the two molecular orientations of H<sub>2</sub>—parallel and perpendicular to the surface. For an orientation parallel to the surface, the molecule will encounter an activation barrier on its way


Figure 3.6. A schematic diagram of the Steering or Dynamical Reorientation process.

towards the surface, which it could overcome by having the appropriate translational energy. On the other hand, for an orientation perpendicular to the surface, the molecule will encounter a hard-wall type potential, and, thus, it might not be able to reach the surface at all. Two ways in which *Steering Effect* can reduce the adsorption probability are as follows—

- 1. by shortening the amount of time that the molecule spends in a favorable orientation, or
- 2. by using up some of the translational energy needed to overcome the activation barrier to reorient a molecule approaching the surface with an initially unfavorable orientation to a favorable one.

R-T (Rotational-Translational) Energy Transfer Effect pertains to the effective transfer of rotational energy to translational energy, which occurs due to the stretching of the molecular bond-length near the surface, and leads to a decrease in the rotational constant. This results from the coupling of the rotational motion to the translational motion along the reaction path. This is easily understood if we consider the physical problem in terms of the concept of a reaction path (path of least resistance/hindrance or least potential). From the two PES plots shown in Fig. 2.3, we see that, depending on the orientation of the molecule relative to the surface, there is a big difference in the form of the reaction path. Projecting the reaction path to the abscissa, each point on the reaction path corresponds to a certain H-H(D-D) internuclear distance. Since the rotational constant depends on the internuclear distance, there is coupling between rotational motion and the motion along the reaction path. In Fig. 3.7, we see that as the molecule approaches the surface, there



Figure 3.7. A schematic diagram of the Rotational-Translational Energy Transfer or the Rotational Assistance via Bond-Length Extension process.

is an increase in its internuclear distance from an initial gas-phase value of  $r_0$  to r(s) (cf., Eq. (2.3)), which leads to an increase in the moment of inertia (cf., Eq. (2.10)), and a decrease in the rotational energy, due to a decrease in the rotational constant (cf., Eq. (2.9)). Assuming that no rotational excitations occur, energy conservation requires that the rotational energy loss ( $\Delta E_j$  in Fig. 3.7) be transferred to the incidence translational energy  $E_t$  (Fig. 3.7), which would then aid in overcoming the activation barrier.

The non-monotonic dependence of the dissociative adsorption of  $D_2$  on Cu(111) on the initial rotational state j of the impinging  $D_2$ , for a fixed incidence energy  $E_t$ , is due to these two factors working for and against the dissociative adsorption process. For low initial rotational states j, because of the somewhat small rotational energy, *Steering Effects* are dominant. As the molecule approaches the surface, it is steered to different regions of the anisotropic PES. Whether or not it will reach a point of relatively low potential on time determines whether the molecule will be adsorbed or not. In terms of the molecule, the anisotropic PES will reorient the molecule on its way towards the surface. The length of time that it stays in a favorable orientation also determines whether it will be adsorbed or not. For high initial rotational states j, the molecule has sufficient rotational energy to assist in sticking, and to the surface the molecule becomes a *blur*. (In some sense, the surface cannot distinguish in which orientation the molecule is.)

#### 3.1.2 Incidence Energy Dependence

We show in Fig. 3.8 the calculated sticking probability curves for the  $D_2/Cu(111)$  system as a function of the initial rotational state of the impinging  $D_2$  molecule for various incidence translational energies  $E_t$ . We can see in Fig. 3.8 that the location of the minimum for each sticking probability curve shifts as the incidence



Figure 3.8. Numerical results for the initial rotational state j-dependent sticking probability curves for D<sub>2</sub> in the vibrational ground state and fixed incidence energies,  $E_t$ . Arrows point to the corresponding minima for each curve. The gas phase rotational constant of D<sub>2</sub> is  $B \approx 3.8$  meV. From [85].  $\diamond: E_t = 0.55$ eV, filled  $\diamond: E_t = 0.575$ eV,  $\Box: E_t = 0.60$ eV, filled  $\Box: E_t = 0.625$ eV,

 $\Delta: E_t = 0.65 \text{ eV}$ , filled  $\Delta: E_t = 0.675 \text{eV}$ ,  $\bigcirc: E_t = 0.70 \text{ eV}$ , filled  $\bigcirc: E_t = 0.80 \text{eV}$ .

energy is varied. This could be understood as follows—When the incidence energy is comparable to or lower than the minimum energy barrier  $V_{min}$ , Steering will not be sufficient to aid in dissociation. Thus, R-T energy transfer will dominate and we see only an increase in the sticking probability as the initial rotational state is increased for low incidence energies (cf., e.g., curves corresponding to 0.55 eV and 0.6 eV in Fig. 3.8). As the incidence energy is gradually increased, the efficacy of Steering also increases and we see corresponding minima appearing (cf., curves corresponding to 0.575 ~ 0.625 eV in Fig. 3.8), that shift towards higher initial rotational states. As the incidence energy is increased to a value that becomes comparable with the energy barrier maximum  $V_{max}$ , the efficacy of R-T energy transfer increases and we see a corresponding shift in the curve minimum towards lower initial rotational states (cf., curves corresponding to 0.80 eV and 0.60 eV in Fig. 3.8).

#### 3.1.3 Isotope Effects

In Figs. 3.9 & 3.10 we show the corresponding  $S_j$  vs. j curves for a H<sub>2</sub> impinging a Cu(111) with fixed incidence translational energies  $E_t$ . We can immediately observe strong isotope effects when we compare our calculation results for the dissociation of D<sub>2</sub>/Cu(111) (Figs. 3.5 & 3.8) with those for H<sub>2</sub>/Cu(111) (Figs. 3.9 & 3.10). For the same incidence energy  $E_t$ , we can immediately see that the locations of the minima for the sticking probability curves of D<sub>2</sub> are shifted more towards higher rotational



Figure 3.9. Sticking coefficient  $S_j$  as a function of the initial rotational state j of a H<sub>2</sub> impinging a Cu(111). (a) m-resolved (b) summed over all m ( $\alpha = 1.5 \text{ Å}^{-1}$ ,  $\beta = 0.25$ ,  $E_a = 0.536 \text{ eV}$ ,  $V_1 = 1.0 \text{ eV}$ ,  $E_t = 0.60 \text{ eV}$ ). The gas phase rotational constant of H<sub>2</sub> is  $B \approx 7.6 \text{ meV}$ .

states  $(j = 5 \rightarrow 8)$  (Fig. 3.8) as compared to those of H<sub>2</sub>  $(j = 4 \rightarrow 5)$  (Fig. 3.10), with H<sub>2</sub> exhibiting higher sticking probabilities than D<sub>2</sub> in the high j region. Because D<sub>2</sub> travels at a much lower velocity than H<sub>2</sub>, even for the same translational energy  $E_t$ , Steering will be more effective for D<sub>2</sub> than for H<sub>2</sub>. Thus, we see that the sticking probability curves for D<sub>2</sub>, when m = 0, (Fig. 3.5(a), m = 0 curve) have higher values as compared to the corresponding sticking probability curves for H<sub>2</sub>, when m = 0, (Fig. 3.9(a), m = 0 curve). This implies that, for the same translational energy



Figure 3.10. Numerical results for the initial rotational state j-dependent sticking probability curves for H<sub>2</sub> in the vibrational ground state and fixed incidence energies,  $E_t$ . Arrows point to the corresponding minima for each curve. The gas phase rotational constant of H<sub>2</sub> is  $B \approx 7.6$  meV.  $\diamond: E_t = 0.55$ eV, filled  $\diamond: E_t = 0.575$ eV,  $\Box: E_t = 0.60$ eV, filled  $\Box: E_t = 0.625$ eV,

 $\Delta: E_t = 0.65 \text{ eV}$ , filled  $\Delta: E_t = 0.675 \text{eV}$ ,  $\bigcirc: E_t = 0.70 \text{ eV}$ , filled  $\bigcirc: E_t = 0.80 \text{eV}$ .

 $E_t$ , the Steering Effect is more successful in reorientating an initially unfavorably oriented D<sub>2</sub> than a H<sub>2</sub>. Since H<sub>2</sub> travels at a much higher velocity than D<sub>2</sub>, it will not have as much time as D<sub>2</sub> to reorient to a favorable orientation and, thus, avoid the activation barrier. Furthermore, D<sub>2</sub> has a smaller rotational constant than H<sub>2</sub> and, thus, will need higher j states before the *R-T energy transfer* could dominate and for the sticking probability curve to increase again in the higher j region. Thus, we observe that the minima of the sticking probability curves for D<sub>2</sub> (Fig. 3.8) are shifted more towards higher j than those for H<sub>2</sub> (Fig. 3.10).

### **3.2** Dynamic Surface

Another interesting question is the effect of surface temperature on the dissociative adsorption process. Recent examinations [25, 32, 105, 107] of the wide range of available experimental data for hydrogen (deuterium) on Cu systems suggest that, in order to consistently relate desorption measurements to direct adsorption experiments via the principle of detailed balance, the adsorption probabilities should show surface temperature dependence. Their results show (for fixed initial vibrational state) a sticking probability that increases with surface temperature in the low incidence energy region, and decreases with increasing surface temperature in the high incidence energy region (cf., Fig. 3.11), without a change in the energetic location of the inflection point of the corresponding adsorption/sticking probability curve.



Figure 3.11. Experimental surface temperature dependent adsorption probabilities for  $D_2$  in the vibrational ground state. The curves were obtained by plugging-in experimental data of Michelsen *et al.* [31,32] into their proposed functional form for the sticking coefficient, and assuming a *j*-independent normalization factor (A = 1) [31], with a surface temperature dependent transition region width [25]. From [82].

This surface temperature dependence of the sticking probability is another interesting behavior which we studied. With the aid of the model system presented in Fig. 2.6, we did quantum mechanical calculations using the coupled-channel method [64], the concept of a local reflection matrix [79], and considering the coupling between the rotational degree of freedom of the molecule and the vibrational degree of freedom of the surface lattice. Our orientationally anisotropic model potential is again based on qualitative features of available PES plots for  $H_2(D_2)/Cu$ surface systems (cf., e.g., [36, 57-61]), with the surface atoms modeled as locally independent Einstein oscillators. We show that this Surface Recoil Effect (effect of allowing the surface atoms to move periodically about their equilibrium position) not only changes the effective height of the activation barrier (due to a transfer/loss of available energy needed to overcome the barrier to dissociation to surface vibrations), it also changes the effective width of the activation barrier to dissociation (Fig. 3.12). From §3.1 we already know that the orientational dependence of the reaction introduces two competing factors [31, 36, 73, 74, 106] working for the dissociative adsorption process, viz., energy transfer (from translation to rotation and vice-versa) effect and Steering Effect. The Steering Effect, which is due to the anisotropic nature of the PES, dominates over the energy transfer effect for low initial rotational states j. For high j, the R-T Energy Transfer Effect, which arises from the strong coupling between the rotational motion and the (translational) motion along the reaction path, dominates.

Upon considering the coupling between these three effects, viz., Steering, Energy



Figure 3.12. A schematic diagram showing a vibrating activation barrier, which, in effect, corresponds to either a narrow activation barrier, or a wide activation barrier.

Transfer, and Surface Recoil, we observed only a very small shift in the energetic position of the inflection point of the adsorption curves determined by using a dynamic surface, as compared to adsorption curves determined by using a rigid surface, when the impinging molecule is initially in its rotational ground state and restricted to be in its vibrational ground state throughout the reaction process. This differs with earlier studies [103, 104, 108] made, where the surface motion was coupled to the intra-molecular vibration. They all observe a considerable shift in the energetic location of the inflection point of the adsorption curves obtained from calculations using a dynamic surface as compared to those using a rigid surface. We think this shift in the energetic location of the inflection point of the adsorption curve might be due to the big difference in the time scales between the intra-molecular vibration and the surface lattice vibration. As a result, the impinging molecule does not feel any effect from the motion of the surface other than an effective increase in the barrier height (or a loss of available translational energy, needed to overcome the activation barrier, to surface motion). Furthermore, we ascribe the broadening of the transition region (region where the adsorption probability changes from 0 to 1) of the adsorption curve, with increasing surface temperature, to the narrowing of the effective width of the activation barrier. (Although the Surface Recoil Effect results in a change in the effective width of the activation barrier to dissociation, as shown in Fig. 3.12, only the narrowing part will qualitatively account for the experimental results.)



Figure 3.13. Comparison between the adsorption probability curves derived from: a rigid surface and considering 5-even rotational channels (filled O); a dynamic surface initially in its ground state and considering 5-even rotational channels and 20-surface vibrational channels; a dynamic surface with 1-even rotational channel and 20-surface vibrational channels. The dynamic surface is taken to be initially in its ground state (n=0) or, in its, first-, second-, third-, fourth-excited states (n=1,2,3,4, respectively). (Initial rotational state j = 0 for all curves.) ( $V_0 = 0.536$  eV,  $V_1 = 1.0$  eV,  $\beta = 0.25$  and, in this figure,  $\alpha = 1.5$  Å<sup>-1</sup>). From [82].

#### 3.2.1 Surface Recoil Effect

In Fig. 3.13 we show a comparison between the adsorption/sticking probability curves for different situations. At the leftmost (filled  $\bigcirc$ s), we show the adsorption probability curve for the case when an impinging molecule reacts with a rigid surface. Relative to this curve (filled  $\bigcirc$ s) is a cluster of curves in the rightmost part (marked by filled  $\Box$ s,  $\Delta$ s, filled  $\Delta$ s,  $\bigcirc$ s, and concentric  $\bigcirc$ s). These are the resulting curves when an impinging molecule reacts with a dynamic surface (introducing the Surface *Recoil Effect*) with different initial surface oscillator states (given by the ns), and suppressing the coupling between the different rotational states of the impinging molecule. (This was done by choosing a single effective activation barrier height, which is the average of all potentials corresponding to all possible orientations.) We can immediately see that, regardless of the initial state of the surface oscillator, the energetic location of the inflection point of this cluster of adsorption curves (rightmost part of Fig. 3.13) does not change. Furthermore, in the low incidence energy region, impinging molecules hitting surface oscillators with high initial states have higher sticking probability as compared to those hitting surface oscillators with lower initial states. On the other hand, in the high incidence energy region, impinging molecules hitting surface oscillators with low initial states have higher sticking probability as compared to those hitting surface oscillators with higher initial states.



Figure 3.14. Comparison of reflection coefficient R, vs. the final surface oscillator state n', curves with (a), (b) fixed initial surface oscillator state, and different incidence energies of the impinging molecule; (c), (d) fixed incidence energy of the impinging molecule, and different initial surface oscillator state and considering 20-surface vibrational channels and only 1-rotational channel. ( $V_0 = 0.536 \text{ eV}$ ,  $V_1 = 1.0 \text{ eV}$ ,  $\beta = 0.25$ , and in this figure  $\alpha = 1.5 \text{ Å}^{-1}$ ). From [82].

In Fig. 3.14, we show the corresponding reflection coefficients for the cluster of adsorption curves mentioned above. For fixed initial surface oscillator states (cf., Figs. 3.14(a) & 3.14(b)), we see a decrease in the number of reflected molecules (proportional to the area under the corresponding reflection curve) as the incidence energy is increased. This is because the molecules gain more translational energy



Figure 3.15. (a),(b) Comparison between the reflection coefficient R, vs., final surface oscillator state n'. Curves derived from a dynamic surface and neglecting (O) rotation, or (filled O) considering rotation. ( $V_0 = 0.536 \text{ eV}$ ,  $V_1 = 1.0 \text{ eV}$ ,  $\beta = 0.25$ , and in this figure  $\alpha = 1.5 \text{ Å}^{-1}$ ). From [82].

to overcome the activation barrier to dissociation. For fixed incidence energy and varying initial oscillator states (cf., Figs. 3.14(c) & 3.14(d)), we see that in the low incidence energy region, high initial surface oscillator states result in more impinging molecules being adsorbed. On the other hand, in the high incidence energy region, high initial surface oscillator states result in fewer impinging molecules being adsorbed. This can be ascribed to the narrowing of the effective width of the activation barrier (Fig. 3.12). Because of Surface Recoil Effect, part of the available



Figure 3.15. (c),(d) Comparison between the reflection coefficient R, vs., final rotational state of reflected molecules j'. Curves derived from (O) a rigid surface, and a (filled O) dynamic surface. ( $V_0 = 0.536 \text{ eV}$ ,  $V_1 = 1.0 \text{ eV}$ ,  $\beta = 0.25$ , and in this figure  $\alpha = 1.5 \text{ Å}^{-1}$ ). From [82].

translational energy needed to overcome the barrier to dissociation is lost to surface oscillator excitations, resulting in motion of the activation barrier along the reaction path. This (virtual) motion of the activation barrier causes its effective width to increase and decrease. In the low incidence energy region, where, classically, the molecule of the system cannot overcome the activation barrier, the narrowing of the activation barrier, during part of the time that the reaction takes place, increases the chance for the molecule of the system to tunnel through the barrier. In the intermediately high incidence energy region (region where the difference between the translational energy of the impinging molecule and the activation barrier height is small), where, classically, the molecule of the system is sure to overcome the activation barrier, the narrowing of the activation barrier, during part of the time that the reaction takes place, decreases the chance that there is an integral number of half-wavelengths of the wave (representing the impinging molecule) that is inside the region of influence of the activation barrier (a quantum mechanical condition for full transmission). And this results in a decrease in the adsorption/sticking probability. For even higher incidence energies, apart from a continuous lost of translational energy to excite the surface, the molecule of the system will not feel the motion of the surface.

The adsorption curve of the impinging molecule derived from a dynamic surface with fixed initial rotational state (j = 0) does not show as much shift in the energetic location of the inflection point as compared to the adsorption curve derived from the same dynamic surface but, with the rotational degree of freedom of the impinging molecule suppressed (cf., Fig. 3.13). This indicates that the inclusion of the rotational degree of freedom of the impinging molecule suppresses the Surface Recoil *Effect.* This is shown in Fig. 3.15(a) (Fig. 3.15(b)) as a decrease (increase) in the area under the reflection curve (filled  $\bigcirc$ ) (for the case when the molecular-rotational degree of freedom is coupled to the surface vibrational degree of freedom) compared to that of the reflection curve  $(\bigcirc)$  (for the case when the molecular-rotational degree of freedom is suppressed). Eventually (cf., Figs. 3.13 and 3.15(b)), the sticking probability derived from a dynamic surface, with the inclusion of molecular rotation, approaches the adsorption curve derived from a rigid surface. This is because, apart from a feeding of translational energy to the surface oscillator (resulting in a virtual increase in activation barrier height), inclusion of molecular rotation allows for a further increase in the activation barrier height, depending on the ability of the PES to reorient the impinging molecule. On the other hand, the Surface Recoil Effect has negligible effect on the rotational excitation of the reflected molecules as shown by the same position of the reflection peaks along the abscissa (cf., Figs. 3.15(c)) and 3.15(d), ( $\bigcirc$ ): rigid surface (filled  $\bigcirc$ ):dynamic surface).

# **3.3** Steering, Energy Transfer, and Surface Recoil Effects

Based on physical arguments, our numerical results, and earlier studies on the subject we conclude that, to properly consider the *Surface Recoil Effect*, it is necessary to take into account the coupling between the internal rotational degree of freedom of the impinging molecule and the surface vibrational degree of freedom. This is contrary to conventional belief that, because of the time scale difference between the internal rotational degree of freedom and the internal vibration degree of freedom of the impinging molecule, it is a good simplification to neglect the internal rotational degree of freedom when studying *Surface Recoil Effects*.

We already know that as a molecule approaches the metal surface, it encounters a PES that is orientation-dependent [26,36,58,59]. In order for the molecule to dissociate and be adsorbed on the metal surface, it must be able to find the path of least

resistance (path of least potential), and have enough energy to reach the surface. This process depends on what the initial state of the impinging molecule is, what its incidence energy is, and how long it stays under the influence of the anisotropic PES [36]. Thus, the rotational degree of freedom plays a vital role in the dissociative adsorption process. In the case of rotation, there are two competing factors working for the dissociation process, viz., Steering and Energy Transfer Effect. The first, Steering Effect, pertains to the orientational dependence of the reaction. The second, Energy Transfer Effect, pertains to the effective transfer of rotational energy to translational energy. This results from the coupling of the rotational motion to the translational motion along the reaction path [36,74]. The non-monotonous behavior [31] of the rotational dependence of the translational dependence of dissociative adsorption of  $D_2$  on Cu(111) can be ascribed to these two competing factors working for the dissociative adsorption process. For low initial rotational states, because of the somewhat small rotational energy, Steering Effect dominates. For high initial rotational states, because the molecule has sufficient rotational energy to assist in sticking, R-T Energy Transfer Effect dominates.

(In this study, where we considered the impinging molecule to be initially in its rotational ground state, the *Steering Effect* dominates. Thus, most of the difference we find between results obtained by suppressing or including rotational motion can be ascribed to the *Steering Effect*.)

The coupling of the translational degree of freedom of the impinging molecule with the vibrational degree of freedom of the surface introduces the Surface Recoil Effect. We have shown ( $\S2.2.1$ ) that the vibration of the surface oscillators normal to the surface plane causes the projections of the activation barrier peaks positions (for the different PES curves corresponding to different positions of the surface oscillators relative to a fixed reference, Fig. 2.6) to the reaction path curve for a rigid surface  $C_0$ , to move along  $C_0$ . Thus, the impinging molecule encounters an activation barrier that is periodically moving towards and away from it. As a result, the effective width of the activation barrier, which is also an important factor in considering the rotational degree of freedom of the impinging molecule [36], changes. Comparison of the surface temperature dependent sticking probability shown in Fig. 3.11 with results of our previous studies (cf., Fig. 3.14 of [36]) show that the widening of the transition region of the adsorption probability curve, as the surface temperature increases, can be ascribed to a narrowing of the effective activation barrier width, with higher surface temperatures corresponding to narrower activation barriers. In the low energy region, where, classically, the impinging molecule will not stick, a narrow activation barrier increases the chances of the impinging molecule to tunnel through the activation barrier. In the high energy region, where, classically, the impinging molecule is sure to stick, a narrowing of the activation barrier decreases the chance that there is an integral number of half-wavelengths (of the wave representing the impinging molecule) that is inside the region of influence of the activation barrier (a quantum mechanical condition that should be satisfied for full transmission).

As for the big shift in the energetic location of the inflection point of the adsorption curve, derived from a dynamic surface compared to that derived from a rigid surface, observed by previous studies [103,104,108], we think this is due to the incompatibility between the two degrees of freedom considered, viz., internal vibrational degree of freedom of the impinging molecule and the vibrational degree

of freedom of the surface. Incompatibility in the sense that, because of the big difference in the time scales of the molecular vibration and the surface vibration, there is a continuous feeding of translational and vibrational energy to the surface oscillators without the impinging molecule noticing any change in the activation barrier other than a relative increase in the height of the activation barrier. In the case of a coupling between the rotational degree of freedom of the impinging molecule and the vibrational degree of freedom of the surface, the time scales are comparable. Hence, even though there is still a continuous feeding of energy to the surface oscillators (as can be noted by a slight shift in the resulting adsorption curve towards higher incidence energies, cf., Fig. 3.13), because of the comparable time scales, the impinging molecule notices the change in the position of the activation barrier. This motion of the activation barrier changes the effective width of the activation barrier. For surface oscillators with low initial vibrational states, and impinging molecules with initially unfavorable orientations, the previous gain due to Steering Effect, which is able to reorient the impinging molecule to a favorable orientation, will be lost. This is because the effective widening of the activation barrier provides enough time for the PES to reorient the impinging molecule to an unfavorable orientation. And the reverse can be said for surface oscillators with high initial vibrational states, and impinging molecules with initially favorable orientations. For very high initial rotational states of the impinging molecule, this surface recoil effect is expected to be very noticeable again, such that there will again be a considerable shift in the adsorption curve results derived from a dynamic surface relative to one derived from a rigid surface. We will consider this in our succeeding studies. Another interesting question is-"Why normal energy scaling is observed despite recent total energy calculations suggesting a very corrugated Cu surface?" Recent ab-initio energy calculations [58,59] report a change in the height of the activation barrier and its position along the reaction path, depending on the surface sites approached by the impinging molecule. This change in height and position of the activation barrier along the reaction path is of the same magnitude as the change introduced if we consider the rotational degree of freedom of the impinging molecule and allow for surface motion. Thus, if we neglect the rotational degree of freedom of the impinging molecule, as well as the effect of surface temperature, there will be a considerable difference in the adsorption curves derived from a corrugated and a flat surface. (Similar to that observed for the effect of neglecting molecular rotation in considering surface vibration, as shown above.) However, with the inclusion of the rotational degree of freedom of the impinging molecule, the difference in the adsorption curves derived from a corrugated and a flat surface would again be made negligible. Thus, providing us with the probable answer to the above question.

.

# Chapter 4

# Rotational Effects in the Associative Desorption Dynamics of $D_2/Cu(111)$

## 4.1 Consistency between Dissociative Adsorption and Associative Desorption Results

When the adsorption probability of molecules colliding with a surface is independent of the distribution of molecular internal states, orientations, and velocities, equilibrium statistical mechanics predicts that the molecular quantum state distributions in the corresponding reverse process of desorption will be determined solely by the surface temperature  $T_S$ . However, this is often not the case, as we have here for the hydrogen on Cu system. Thus it would also be interesting to study how the desorption probability (the probability that D atoms initially chemisorbed on the Cu surface come together and detach from the surface as D<sub>2</sub> molecules) will behave, as such studies could elucidate the nature of those special forces and configurations experienced by the desorption flux when we relate them to the adsorption probabilities.

We did quantum mechanical calculations [33, 34, 36, 79, 82, 85] of the desorption probability, independent of the adsorption probability results, by invoking the principle of microscopic reversibility [33, 34] and solving the time-independent Schrödinger equation for a  $D_2$  molecule moving along the reaction path, and under the influence of an orientationally anisotropic potential energy surface (PES) based on qualitative features of available PES plots for the  $H_2$  on Cu(111) surface system [36, 57, 58]. As described in Chapter 2, the dynamical variables we have considered are the translational and vibrational coordinates of the desorbing molecule, which are represented by the reaction coordinates s and r, respectively, and the polar and azimuthal angular orientation of the molecule with respect to the surface, which are represented by  $\theta$  and  $\varphi$ , respectively. The energy barrier for a parallel-oriented D<sub>2</sub> molecule was set at  $V_{min} = V_{\parallel} \approx 0.5 \text{ eV}$ , and gradually increased to a value  $V_{max} = V_{\perp} \approx 0.9 \text{ eV}$ for a perpendicular-oriented molecule. The form of our orientation-dependent PES results in a selection rule where molecules in even (odd) initial rotational states will end up in even (odd) final rotational states. Furthermore, the azimuthal quantum numbers  $m_i$  are conserved. (Please refer to Chapter 2 and [33, 34, 36, 79, 82] for



Figure 4.1. Boltzmann plot of the D<sub>2</sub> desorption probability vs. rotational energy  $E_j$  of the state j. The line  $T_R = T_S = 925$ K is plotted for reference. The  $\Diamond$ 's correspond to experimental data [31]. The gas phase rotational constant of D<sub>2</sub> is  $B \approx 3.8$  meV. From [85].

more details regarding the calculation method, and the actual form of the model potential adopted.) We then calculated the probability  $D(j, T_S)$  that the molecule desorbs with final rotational state j from a surface at surface temperature  $T_S$  by taking the Boltzmann average of the raw, numerical desorption probability results over the initial energy distribution at surface temperature  $T_S$ . We show in Fig. 4.1 a Boltzmann plot of the resulting desorption probability of D<sub>2</sub> molecules as a function of the rotational energy. A Boltzmann distribution would appear as a straight line (*cf.*, Fig. 4.1). However, we see that the calculated desorption probability result shown in Fig. 4.1 is not represented by a single temperature, and the mean rotational energy is less than  $T_S$  [34]. These qualitative features are also observed experimentally [28, 30-32].

In order to relate the desorption results in Fig. 4.1 to the adsorption probability results in Fig. 3.8, we show, in Fig. 4.2, a Boltzmann plot of our numerical results for the desorption probability of  $D_2$  molecules as a function of the rotational energy for a fixed incidence energy. Recall from the principle of microscopic reversibility, and the conservation of energy [33,34], that the dynamic behavior of the adsorption



Figure 4.2. Boltzmann plot of the D<sub>2</sub> desorption probability vs. rotational energy  $E_j$  of the state j ( $\nu = 0$ ), for fixed translational energy  $E_t = 0.60$  eV. The line  $T_R = T_S = 925$ K is plotted for reference. The gas phase rotational constant of D<sub>2</sub> is  $B \approx 3.8$  meV. From [85].

probability will be reflected in the distribution of molecular quantum states in desorption in the following manner—

$$D(E_t, j) \propto S(E_t, j) \exp\left(-\frac{E_t + E_j}{k_B T_S}\right),$$
(4.1)

where  $E_t$  is the translational energy of the molecule, and j is its rotational state with a corresponding rotational energy  $E_j$ . The initial decrease in the sticking probability curve corresponding to an incidence energy of  $E_t = 0.6$  eV in Fig. 3.8 is reflected as a decrease in the rotational temperature in desorption (Fig. 4.2). The final increase in the sticking probability curve is reflected as an increase in the rotational temperature relative to the former decrease. Note that the increase in rotational temperature is not as dramatic as that expected from the corresponding sticking probability curve in Fig. 3.8. This is because the Boltzmann factor in Eq. (4.1) decreases much more rapidly compared to the increase in the sticking probability. If we then sum over all the incidence energies, we get the Boltzmann plot shown in Fig. 4.1, where the initial decrease in the rotational temperature with respect to the surface temperature for low rotational energies,  $E_j \leq 0.05$  eV, is due to an initial mean decrease in the sticking probability for low initial rotational states, and the mild increase in the rotational temperature for higher rotational energies, 0.05 eV  $\leq E_j \leq 0.5$  eV, is due to a mean increase in the sticking probability for higher initial rotational states (cf., Fig. 3.8 and Fig. 4.1). The final decrease again of the rotational temperature can be understood by considering the result shown in Fig. 4.2 and the relation between the sticking probability and the desorption probability (Eq. (4.1)). As the rotational energy  $E_j$  appearing in the Boltzmann factor increases, the only relevant contributions will come from the sticking probabilities corresponding to those incidence energies  $E_t \ll V_{min}$ . In this energy region, the sticking probabilities are not much different from 0, even for j = 14. As a result, we will observe this final decrease in the rotational temperature for the desorption probability of hydrogen molecules in their vibrational ground state ( $\nu = 0$ ).

# 4.2 Rotational Alignment & Dynamical Quantum Filtering

To demonstrate how surfaces that adsorb hydrogen could act as rotational quantum state filters, and cause desorbing hydrogen molecules to exhibit rotational alignment, we again considered the reaction of a D<sub>2</sub> molecule with a Cu(111) surface, and calculated for the corresponding desorption probability, as described in §4.1 and Chapter 2. For a given total kinetic energy  $E_{tot}$  (defined as the sum of the final translational energy  $E_t$  and the final rotational energy  $E_j$  of the molecule after desorption,  $E_{tot} = E_t + E_j$ ), we calculated for the  $m_j$ -resolved probability  $D_{jm_j}(E_{tot})$  that the molecule desorbs with final rotational state  $(j, m_j)$ , where molecules with azimuthal quantum number  $|m_j| = j$  have their rotational axes oriented, predominantly, perpendicular to the surface (helicopter-type rotation), molecules with  $m_j = 0$  have their rotational axes oriented, predominantly, parallel to the surface (cartwheel-type rotation), and molecules with  $0 < |m_j| < j$  have their rotational axes oriented intermediate between the two former ones. From these calculated desorption probabilities  $D_{jm_j}(E_{tot})$ , we calculated for the corresponding quadrupole alignment factors

$$A_0^{(2)}(j) = \frac{\sum_{m_j} [3m_j^2 - j(j+1)] D_{jm_j}(E_{tot})}{j(j+1) \sum_{m_j} D_{jm_j}(E_{tot})}.$$
(4.2)

The quadrupole alignment factor  $A_0^{(2)}(j)$  gives us an insight as to the degree of alignment and orientation preference of the desorbing D<sub>2</sub> molecules, and assumes values in the range [-1, 3j/(j+1) - 1]. For molecules exhibiting cartwheel-type rotations  $(|m_j| \approx 0)$  with respect to the surface normal  $\hat{n}$ ,  $A_0^{(2)}(j) < 0$ , while those exhibiting helicopter-like rotations  $(|m_j| \approx j)$  have  $A_0^{(2)}(j) > 0$ , with perfect alignment given by  $A_0^{(2)}(j) = 3j/(j+1) - 1$ , and as  $j \to \infty$ ,  $A_0^{(2)}(j) \to 2$ . A spatially isotropic distribution of the angular momentum **j**-vector is described by  $A_0^{(2)}(j) = 0$ .

In Fig. 4.3 we show the calculated  $A_0^{(2)}(j)$  results for D<sub>2</sub> molecules desorbing in the vibrational ground state ( $\nu = 0$ ) from Cu(111), with total kinetic energy  $E_{tot} = 0.40 \rightarrow 1.00$  eV. We can see that for total kinetic energies lower than the minimum translational barrier height ( $E_{tot} < V_{min} = V_{\parallel} \approx 0.5$  eV, Fig. 4.3), there is



Figure 4.3. Rotational alignment for D<sub>2</sub> molecules desorbing in the state ( $\nu = 0, j, E_{tot}$ ) from Cu(111) as a function of the final rotational state j. Total kinetic energy  $E_{tot} = 0.40 \rightarrow 0.90$  eV.

Table 4.1. The list shows the estimated maximum final rotational state  $j_{max}$  accessible to the desorbed D<sub>2</sub> molecules and the corresponding rotational energy  $E_{j_{max}} = B_{j_{max}}(j_{max} + 1)$  for fixed final total kinetic energies  $E_{tot}$ . Also shown are the corresponding estimated critical rotational states  $j_{crit}$ . The rotational constant of D<sub>2</sub> in the gas phase is taken to be  $B \approx 3.8$  meV, and  $V_{min} = V_{\parallel} \approx 0.5$  eV. From [89].

Etot[meV]	$E_{j_{mex}}$ [meV]	jmax	jcrit	
100	76	4	0	
200	160	6	0	
300	274	8	0	
400	342	9	0	
500	418	10	1	
600	593	12	3	
700	692	13	6	
800	798	14	8	
900	798	14	10	
1000	921	15	10	

a general preference for cartwheel-type rotations. As  $E_{tot}$  increases, we eventually see an emerging preference for helicopter-type rotations ( $E_{tot} \ge V_{min} = V_{\parallel} \approx 0.5 \text{ eV}$ , Fig. 4.3). We can also immediately see that, for a particular total kinetic energy  $E_{tot}$ ,  $A_0^{(2)}(j)$  is a nonmonotonic function of the detected final rotational state j. Furthermore, this nonmonotonic behavior is strongly dependent on the translational energy  $E_t$  (cf., Figs. 4.4 & 4.5). These observations are quite understandable if we keep three things in mind. First, associative desorption is a strongly orientation dependent process, where molecules oriented parallel to the surface are favored to



Figure 4.4. Rotational alignment for D<sub>2</sub> molecules desorbing in the state ( $\nu = 0, j, E_t$ ) from Cu(111) as a function of the final translational energy  $E_t$ . Final rotational state  $j = 1 \rightarrow 7$ . Surface temperature  $T_S = 950$  K. From [89].

perpendicular-oriented molecules. Second, when hydrogen molecules are found adsorbed on the surface, there is essentially no such thing as a rotational state, nor does an initial orientation have meaning. Third, the maximum final rotational state  $j_{max}$  accessible to the desorbed molecules is limited by the available total kinetic energy  $E_{tot}$  (Table 4.1).

On the way towards the gas phase, desorbing molecules are bound to follow the path of least resistance (path of least potential). Since the initial rotational state  $j_{ad}$  of molecules about to form from adsorbed atoms may take any value, and we may assume that these molecules are then initially oriented parallel to the surface  $(|m_{j_{ad}}| \approx j_{ad})$ , all molecules will try to desorb. However, on crossing the transition region towards desorption, the metal surface, via the orientation-dependent PES, acts as a sort of rotational quantum state filter/sieve, and filters out all rotational states  $j_{des}$  greater than some critical rotational state  $j_{crit}$ , which depends on the relative value of  $E_{tot}$  with respect to  $V_{min}$ . As a result, upon desorption, only those molecules with rotational state  $j_{des} \leq j_{crit}$  will survive. Given  $V_{min}$  and  $E_{tot}$ , we can roughly estimate  $j_{crit}$  and  $j_{max}$  by calculating for the corresponding energies  $E_{j_{crit}}$ and  $E_{j_{max}}$ . (When  $[E_{tot} - V_{min}] > 0$ ,  $E_{j_{crit}} \approx [E_{tot} - V_{min}]$ , otherwise  $E_{j_{crit}} = 0$ .  $E_{j_{max}} \approx E_{tot}$ ). For D<sub>2</sub>, the approximate values of  $j_{crit}$  and  $j_{max}$  for a particular value of  $E_{tot}$  are listed in Table 4.1. Furthermore, it should be noted that, since the path of *least resistance* (path of least potential) will be favored over all other possible paths, as  $j_{des} \rightarrow j_{crit}$ , a majority of those molecules that did survive the attempt to desorb will exhibit helicopter-like rotations (*i.e.*,  $|m_{j_{des}}| \approx j_{des}$ ). This is easily understood if we recall that a sufficient translational energy is required to, at least, overcome



Figure 4.5. Rotational alignment for D<sub>2</sub> molecules desorbing in the state ( $\nu = 0, j, E_t$ ) from Cu(111) as a function of the final translational energy  $E_t$ . Final rotational state  $j = 8 \rightarrow 14$ . Surface temperature  $T_S = 950$  K. From [89].

the barrier minimum  $V_{min}$ . Suppose a molecule that did survive the attempt to desorb assumes a rotational state  $j_{des} \approx j_{crit}$  upon desorption. With a fixed total energy  $E_{tot}$ , it will only have just enough translational energy to overcome the barrier minimum  $V_{min}$ , which requires that the desorbing molecule exhibits helicopter-like rotation  $(|m_{jdes}| \approx j_{des})$ .

Upon desorption, we find the molecules in the state  $(j_{des}, m_{j_{des}})$ , where  $|m_{j_{des}}| \leq$  $j_{des} \leq j_{crit} \leq j_{max}$ . The desorbed molecules then assume a final rotational state  $(j, m_j)$  by undergoing either rotational excitations  $(j > j_{des})$  or de-excitations  $(j < j_{des})$ , or by remaining in the same rotational state  $(j = j_{des})$ . Those that assume final rotational states  $j < j_{crit}$  are more inclined to exhibit helicopter-like rotations, and those that assume final rotational states  $j > j_{crit}$  are more inclined to exhibit cartwheel-like rotations. For a fixed total kinetic energy  $E_{tot}$ , those that undergo rotational excitation do so at the expense of the translational energy  $E_t$ . By undergoing rotational excitation upon desorption, the molecule assumes a final rotational state  $(j, m_j)$  with  $j > j_{des} \ge |m_{j_{des}}| = |m_j|$  and, thus, we would most likely find these molecules exhibiting cartwheel-like rotations. On the other hand, those that undergo rotational de-excitation will do so with a gain in translational energy  $E_t$ . By undergoing rotational de-excitation, the molecule assumes a final state  $(j, m_j)$  with  $j < j_{des} \ge |m_{j_{des}}| = |m_j|$  and, since  $j \ge |m_j|$  always, we would most likely find these molecules exhibiting helicopter-like rotations. Those that undergo neither rotational excitations nor de-excitations retain the same translational energy  $E_t$  and, as mentioned earlier, we would most likely find these molecules exhibiting helicopter-like rotations, with  $|m_j| = |m_{j_{des}}| \approx j$ .

When the total kinetic energy  $E_{tot}$  is small  $(E_{tot} \leq V_{min})$ ,  $j_{crit} \approx 0 \ll j_{max}$  and, since only those states  $j > j_{crit}$  are accessible as final rotational states, rotational excitations are more likely to occur. Thus, we find the desorbed molecules exhibiting cartwheel-like rotations  $(E_{tot} = 0.4 \rightarrow 0.5 \text{ eV}$  in Fig. 4.3). As the total kinetic energy  $E_{tot}$  increases,  $j_{crit}$  also increases. Now both  $j > j_{crit}$  and  $j < j_{crit}$  are possible final rotational states. When the desorbed molecules assume final rotational states  $j < j_{crit}$ , we find them more inclined to do helicopter-like rotations (cf., low jregion in Fig. 4.3, with  $E_{tot} > V_{min}$ ). As the final rotational state j increases  $(j \rightarrow j_{crit}), A_0^{(2)}(j) \rightarrow 3j/(j+1) - 1$  (perfect alignment), and the rotation becomes more helicopter-like. And when the desorbed molecules assume final rotational states  $j > j_{crit}$ , we find them more inclined to do cartwheel-like rotations (cf., high<math>j region in Fig. 4.3, with  $E_{tot} > V_{min}$ ). When  $E_{tot}$  is large enough  $(E_{tot} \gg V_{min})$ ,  $j_{crit} \rightarrow j_{max}$  and rotational excitations as well as de-excitations are equally possible. We then find the molecules exhibiting an almost orientationally isotropic j-vector distribution, *i.e.*,  $A_0^{(2)}(j) \rightarrow 0$   $(cf., A_0^{(2)}(j = 1 \rightarrow 14)$  for  $E_{tot} = 1.00$  eV in Fig. 4.3).

Because the quadrupole alignment factors  $A_0^{(2)}(j)$  (Eq. (4.2)) are defined for a particular final rotational state j, corresponding to a particular rotational energy  $E_j$ , we can also define the corresponding translational energy  $(E_t-)$  dependent quadrupole alignment factors  $A_0^{(2)}(j)$ , the results of which we show in Figs. 4.4 & 4.5. As expected from previous discussions, D<sub>2</sub> molecules desorbing with translational energies lower than the minimum barrier height  $(E_t < V_{min})$  have correspondingly low total kinetic energies  $E_{tot}$ , and exhibit cartwheel-like rotational preference (cf.,  $E_t < 0.5$  eV region in Fig. 4.4, and  $E_t \leq 0.2$  eV region in Fig. 4.5). As the  $E_t$  increases, corresponding to an increase in  $E_{tot}$ , the rotational preference becomes more helicopter-like (cf.,  $0.5 \leq E_t < 0.6$  eV region in Fig. 4.4, and  $0.2 \leq E_t \leq 0.5$  eV region in Fig. 4.5). When the translational energy is sufficiently large  $(E_t > V_{min})$ , we find the D<sub>2</sub> molecules exhibiting an almost orientationally isotropic j-vector distribution  $(A_0^{(2)}(j) \to 0)$  regardless of the final rotational state (cf.,  $A_0^{(2)}(j = 1 \to 14)$ for  $E_t = 0.80 \rightarrow 0.90$  eV in Figs. 4.4 & 4.5). It should be noted that we also obtained the same general features as that presented here even for the other strongly orientation-dependent reactions between hydrogen molecules and other surfaces. An example is the desorption of  $D_2$  from a Pd-surface [41], which, although it requires an altogether different corresponding set of values for  $V_{min}$  and  $V_{max}$  [40], is also strongly orientation dependent.

So far we have presented alignment factor results without considering the surface temperatures. In Fig. 4.6 we show the results of our calculation for  $A_0^{(2)}(j)$ , averaged over the Boltzmann distribution of total kinetic energies  $E_{tot}$  of the desorbing molecules at the surface temperature  $T_S = 920$  K, *i.e.*,

$$A_{0}^{(2)}(j,T_{S}) = \left\langle \frac{3j_{z}^{2} - j^{2}}{j^{2}} \right\rangle_{j} = \frac{\int dE_{t} \sum_{m_{j}} [3m_{j}^{2} - j(j+1)] D_{jm_{j}}(E_{tot}) e^{-E_{tot}/k_{b}T_{S}}}{j(j+1) \int dE_{t} \sum_{m_{j}} D_{jm_{j}}(E_{tot}) e^{-E_{tot}/k_{b}T_{S}}},$$
(4.3)

(in which a majority of the contribution to this average will come from desorbing molecules with total kinetic energies that are comparable with the barrier minimum, *i.e.*,  $E_{tot} \approx V_{min}$ .) Upon averaging our results over the Boltzmann distribution of



Figure 4.6. Rotational alignment for D<sub>2</sub> molecules desorbing in the state ( $\nu = 0, j$ ) from Cu(111), averaged over the Boltzmann distribution of total kinetic energies at the surface temperature  $T_S = 920$  K.

total kinetic energies of the desorbing molecules at the surface temperature relevant to existing experiments  $(T_S \approx 920 \text{ K} \text{ for Cu } [47,50])$ , we get an alignment factor of  $A_0^{(2)}(j,T_S) \approx 0.3 \rightarrow 0.7$  for  $j = 1 \rightarrow 14$ , corresponding to a small preference for helicopter-like rotation, which qualitatively agrees with experimental results [50]. The small helicopter-like rotation preference is to be expected because, although there are many possible paths to desorption, the *path of least resistance* (path with the lowest energy requirement), corresponding to a parallel orientation (helicopterlike motion), will be strongly preferred over other paths. In terms of an  $m_j$ -resolved desorption probability, because of the Boltzmann factor, only events corresponding to a particular range of  $E_{tot}$ , wherein there is only a slight difference between the results for  $|m_j| = j$  and  $m_j = 0$ , are chosen to contribute to the desorption at the surface temperature  $T_S$ . However, as we have shown here, strong orientational preference in the desorption of hydrogen molecules should be observable with state (j-) and energy  $(E_{tot}-$  or  $E_t-$ ) resolved mesurements.

It would also be interesting to see how a higher-dimensional description, which includes surface corrugations and surface oscillations, will affect the results we have presented here. However, given the relatively high surface temperatures considered in experimental measurements [30, 31, 41, 47, 50], we expect to see only slight surface corrugation effects. Furthermore, as mentioned above, the desorbing molecules are bound to follow the *path of least resistance* (path with the lowest energy requirement), and thus, we believe that a high-dimensional description will still show the same general features we have presented here.

We have shown that the metal surface, via the orientation-dependent PES, can



Figure 4.7. Comparison between the rotational alignments of D<sub>2</sub> ( $\diamond$ ) [88] and H<sub>2</sub> (filled  $\diamond$ ) desorbing in the state ( $\nu = 0, j$ ) from Cu(111), averaged over the Boltzmann distribution of total kinetic energies at the surface temperature  $T_S = 920$  K.  $\Box$  and O: experimental results for D<sub>2</sub>( $\nu = 0, j, T_S = 920$  K) using REMPI detection with P and R branch transitions, respectively [50]. Filled  $\triangle$ : experimental results for D<sub>2</sub>( $\nu = 0, j, T_S = 950$  K) using LIF detection [47]. From [90].

act as a rotational quantum state filter, and cause desorbing hydrogen molecules to exhibit rotational alignment. We have also shown that the resulting alignment of the desorbed molecules, as determined by the value of the quadrupole alignment factors  $A_0^{(2)}(j)$ , exhibits a nonmonotonic j- and  $E_t$ - dependence, similar to the dependence of the adsorption probability of a hydrogen molecule, impinging a Cu(111) surface, on its initial rotational state [30,31,36] and initial translational energy [85]. Thus, we could, e.g., permeate H(D) atoms through the bulk of a copper single crystal and use the Cu(111) surface as a dynamical quantum filter to produce oriented H<sub>2</sub>(D<sub>2</sub>) molecules. As shown in Figs. 4.4 & 4.5, all we have to do is devise a means to either select only slow desorbing ( $E_t \ll V_{min}$ ) molecules or fast desorbing ( $E_t > V_{min}$ ) molecules, and get, respectively, either perpendicular-oriented or parallel-oriented molecules.

#### 4.3 Isotope Effects

In Fig. 4.7 we show the calculated  $A_0^{(2)}(j, T_S)$  results for H<sub>2</sub> and D<sub>2</sub> desorbing in the vibrational ground state ( $\nu = 0$ ) from Cu(111), averaged over the Boltzmann distribution of total kinetic energies at the surface temperature  $T_S = 920$  K. For reference, we have also replotted the experimental results of Zacharias' [47] and Auerbach's [50] group, for D<sub>2</sub> desorbing in the vibrational ground state ( $\nu = 0$ ) from

Table 4.2. The list shows the corresponding estimated critical rotational states  $j_{crit}$ , the maximum final rotational state  $j_{max}$  accessible to the desorbed  $H_2(D_2)$ , and the corresponding rotational energy  $E_{j_{max}} = B_{j_{max}}(j_{max}+1)$  for fixed final total kinetic energies  $E_{tot}$ . The rotational constant of  $H_2(D_2)$  in the gas phase is taken to be  $B \approx 7.6(3.8)$  meV, and  $V_{min} = V_{\parallel} \approx 0.5$  eV.

ш.	$E_{tot}[meV]$	*	500	600	700	800	900	1000
n <sub>2</sub>	$E_{j_{max}}[meV]$	≈	425	547	684	684	836	836
	jmax	~	7	8	9	9	10	10
	Ĵcrit	≈	1	2	4	6	7	8
$D_2$								
	$E_{imax}$ [meV]	~	418	593	692	798	798	912
	jmax	≈	10	12	13	14	14	15
	Ĵcrit	~	1	3	6	8	10	
D <sub>2</sub>	E <sub>jmex</sub> [meV] jmax jcrit	* * *	418 10 1	593 12 3	692 13 6	798 14 8	798 14 10	912 15 10

Cu(111), with surface temperatures  $T_S = 950$  & 920 K, respectively. The slightly lower results of Zacharias *et al.* [47] may, in part, be due to surface temperature  $T_S$ effects. Earlier studies ([82] and references found therein) have shown that, for a particular initial rotational state and low collision energies, an increase in  $T_S$  results in an increased dissociation, which can be associated with a decrease in effective dissociation barrier and, in turn, a decrease in the orientational anisotropy of the PES. Applying the principle of microscopic reversibility [33,34], an increase in  $T_S$ will result in decreased alignments (Fig. 4.7).

We can see that within the limits of the experimental error bars, our results qualitatively agree with experiments, and show small preference for helicopter-like rotation. We got  $A_0^{(2)}(j = 1 \rightarrow 14, T_S = 920 \text{ K}) \approx 0.3 \rightarrow 0.7$ , as compared to experimental measurements of  $A_0^{(2)}(j = 1 \rightarrow 7, T_S = 950 \text{ K}) \approx 0 \rightarrow 0.1$  [47] and  $A_0^{(2)}(j = 1 \rightarrow 11, T_S = 920 \text{ K}) \approx 0 \rightarrow 0.8$  [50]. We can also see that, for low final rotational states j, the spatial distribution of the angular momentum j-vector of desorbing H<sub>2</sub> is more helicopter-like (has greater  $A_0^{(2)}(j,T_S)$  values) compared to desorbing  $D_2$ . As j increases further, we eventually observe that the j-vector distribution of desorbing H<sub>2</sub> becomes more isotropic (has smaller  $A_0^{(2)}(j,T_S)$  values) compared to desorbing  $D_2$ . To explain this, we recall [88,89] that—The initial rotational state  $j_{ad}$  of molecules about to form from adsorbed atoms may take any value. We may then assume/suppose that these molecules are most likely initially oriented parallel to the surface  $(|m_{j_{ad}}| \approx j_{ad})$ . Upon introducing a certain amount of energy to the system, e.g., by increasing  $T_S$ , all molecules will try to desorb, but not all will necessarily succeed. On their way towards the gas phase, these molecules have to cross a transition region where a sufficient amount of translational energy is necessary to, at least, overcome the barrier minimum  $V_{min}$ . Thus, the metal surface, via the orientation-dependent PES, will act as a sort of rotational quantum state filter/sieve, and filters out all rotational states  $j_{des}$  greater than some critical rotational state  $j_{crit}$ . As a result, only those molecules with rotational state  $j_{des} \leq j_{crit}$  will survive and desorb with final rotational states  $j \leq j_{max}$  (maximum accessible final rotational state, vide infra). Given  $V_{min}$  and  $E_{tot}$ , we can roughly estimate  $j_{crit}$  and  $j_{max}$  by calculating for the corresponding energies  $E_{j_{crit}}$  and  $E_{j_{max}}$ (cf., Table 4.2—when  $[E_{tot} - V_{min}] > 0$ ,  $E_{j_{crit}} \approx [E_{tot} - V_{min}]$ , otherwise  $E_{j_{crit}} = 0$ .  $E_{j_{max}} \approx E_{tot}$ ). For a fixed  $E_{tot}$ , suppose a molecule did survive the attempt to

desorb, and had a rotational state  $j_{des} \approx j_{crit}$  upon desorption. It would mean that the molecule had only just enough translational energy to overcome the barrier minimum  $V_{min}$ , which requires that the molecule exhibits helicopter-like rotation  $(|m_{j_{des}}| \approx j_{des})$  upon desorption. Thus, as  $j_{des} \rightarrow j_{crit}$ , a majority of those molecules that did survive the attempt to desorb will exhibit helicopter-like rotations, *i.e.*,  $|m_{j_{des}}| \approx j_{des}$ . Upon desorption, we find the molecule in the state  $(j_{des}, m_{j_{des}})$ , where  $|m_{j_{des}}| \leq j_{des} \leq j_{crit} \leq j_{max}$ . The molecule will then assume its final rotational state  $(j, m_j)$  by either —

- 1. undergoing rotational excitation  $(j > j_{des} \ge |m_{j_{des}}| = |m_j|)$  at the expense of its translational energy  $E_t$ , or
- 2. undergoing rotational de-excitations  $(j < j_{des} \ge |m_{j_{des}}| = |m_j|)$  with a gain in  $E_t$ , or
- 3. by remaining in the same rotational state  $(j = j_{des} \approx |m_{j_{des}}| = |m_j|)$ and retaining the same  $E_i$ .

Thus, those that assume final rotational states  $j \leq j_{crit}$  are more helicopter-like (have greater  $A_0^{(2)}(j)$  values) compared to those that assume final rotational states  $j > j_{crit}$ . Because the rotational constant of H<sub>2</sub> is greater than that of D<sub>2</sub>, for the same total kinetic energy  $E_{tot}$ , H<sub>2</sub> has lower  $j_{crit}$  compared to D<sub>2</sub> (Table 4.2). As a consequence, we see in Fig. 4.7 that upon averaging over the Boltzmann distribution of total kinetic energies at the surface temperature  $T_S = 920$  K, the spatial distribution of the angular momentum **j**-vector of desorbing H<sub>2</sub> is more helicopter-like (has slightly greater  $A_0^{(2)}(j, T_S)$  values) compared to desorbing D<sub>2</sub>, for low j. And when j is sufficiently large (j > 9), the **j**-vector distribution of desorbing H<sub>2</sub> becomes more isotropic (has smaller  $A_0^{(2)}(j, T_S)$  values) compared to desorbing D<sub>2</sub>.

Because the quadrupole alignment factors  $A_0^{(2)}(j)$  (Eq. (4.2)) are defined for a particular final rotational state j, corresponding to a particular rotational energy  $E_j$ , we can also define the corresponding translational energy  $(E_t-)$  dependent quadrupole alignment factors  $A_0^{(2)}(j)$ . In Fig. 4.8 we show the calculated  $A_0^{(2)}(j)$  results for  $H_2(D_2)$  desorbing in the state ( $\nu = 0, j = 11$ ) from Cu(111). For reference, we have also replotted the experimental results of Auerbach's group [99], for D<sub>2</sub> desorbing in the state ( $\nu = 0, j = 11$ ) from Cu(111). As expected from previous discussions [88,89],  $H_2(D_2)$  desorbing with translational energies lower than the minimum barrier height  $(E_t < V_{min})$  have correspondingly low total kinetic energies  $E_{tot}$ , and exhibit cartwheel-like rotational preference (cf.,  $E_t < 0.3$  eV region in Fig. 4.8). As  $E_t$  increases, corresponding to an increase in  $E_{tot}$ , the rotational preference becomes more helicopter-like (cf.,  $0.3 \le E_t < 0.6$  eV region in Fig. 4.8). When the translational energy is sufficiently large  $(E_t > V_{min})$ , we find the desorbing H<sub>2</sub>(D<sub>2</sub>) exhibiting an almost orientationally isotropic j-vector distribution  $(A_0^{(2)}(j) \rightarrow 0)$ , regardless of the final rotational state [89]. And, as expected, for translational energies that are comparable with the barrier minimum (*i.e.*,  $E_t \approx V_{min}$ ), the j-vector distribution of desorbing H<sub>2</sub> is more helicopter-like (has greater  $A_0^{(2)}(j)$  values) compared to desorbing D<sub>2</sub>. As  $E_t$  increases, the corresponding j-vector distribution of desorbing H<sub>2</sub> eventually becomes more spatially isotropic (has smaller  $A_0^{(2)}(j)$  values) than does the corresponding j-vector distribution of desorbing  $D_2$ . It should be noted that we also obtained the same general features as that presented here even for



Figure 4.8. Comparison between the rotational alignments of D<sub>2</sub> ( $\diamond$ ) [89] and H<sub>2</sub> (filled  $\diamond$ ) desorbing in the state ( $\nu = 0, j = 11, E_t$ ) from Cu(111) as a function of the final translational energy  $E_t$ . Filled  $\triangle$ : experimental results for D<sub>2</sub>( $\nu = 0, j = 11$ ) using REMPI detection [99]. From [90].

the desorption of  $H_2(D_2)$  from a Pd-surface [41], which, although it requires an altogether different corresponding set of values for  $V_{min}$  and  $V_{max}$  (cf., Chapter 5, [40], and references found therein), is also strongly orientation dependent.

The discrepancy in magnitude between our results and that of the experimental measurements may, in part, be due to our flat surface model. However, considering the relatively high surface temperatures considered in actual experiments [47, 50, 99], we expect to see only slight corrugation effects, and a higher-dimensional description that takes into account *all* degrees of freedom will still exhibit the qualitative features we have presented here. Furthermore, aside from the relatively large experimental error bars, background signals arising from molecules that reenter the detection volume after undergoing collisions, which are unpolarized and may decrease measured alignments, may not have been sufficiently accounted for [50, 100, 101], indicating a need for further experimental verifications [100, 101].

# Chapter 5

# Rotational Effects in the Dynamics of Hydrogen on a Pd Surface

# 5.1 Rotational Effects in the Dissociative Adsorption Dynamics

So far, we have been considering the activated  $H_2(D_2)/Cu(111)$  system, which we can associate with an "S"-shaped dissociation probability vs. translational energy curve. However, as expected, not all systems are activated, nor will all show this "S"-shaped dissociation curve. A typical example of such a (non-activated) system is  $H_2(D_2)/Pd(111)$ . In this chapter, we will consider the dissociative adsorption and associative desorption dynamics of  $H_2(D_2)/Pd(111)$ , and see how the dynamics of such a non-activated system compares with the activated  $H_2(D_2)/Cu(111)$  system we considered earlier.

More recent advances in molecular beam scattering techniques have made it possible to determine the initial rotational state of hydrogen molecules prior to being adsorbed on metal surfaces [37-39]. For the H<sub>2</sub>/Pd(111) system, Gostein and Sitz [39] directly observed, for the first time, that the sticking (dissociation) coefficient [35] of  $H_2$  on Pd(111) has a nonmonotonic dependence on the initial rotational state of the impinging  $H_2$  (Fig. 5.1), first decreasing with increasing initial rotational state  $(j = 0 \rightarrow 3)$ , for low j, then increasing again for higher j (j = 4, 5). This interesting feature of the sticking coefficient of  $H_2/Pd(111)$  as a function of the initial rotational state j of the impinging H<sub>2</sub> reminds us of the sticking probability results inferred from rotationally state-resolved time-of-flight (TOF) distribution results of Michelsen et al. [30] for  $D_2$  molecules associatively desorbing from Cu(111). We will show in this chapter that the mechanism behind the nonmonotonic j-dependence observed here can be understood by again taking into account the two competing factors working for the dissociative adsorption process, viz., Steering or the DYNAM-ICAL REORIENTATION factor, and Rotational-Translational Energy Transfer or the ROTATIONAL ASSISTANCE via BOND-LENGTH EXTENSION factor. These factors are similar to the ones observed for the hydrogen on copper system, and come about as a consequence of the orientational dependence of the hydrogen-surface reaction. Another interesting feature we can directly observe from the results of Gostein and



Figure 5.1. Experimental results for the *j*-dependent sticking probability curves for H<sub>2</sub> on Pd(111) for fixed translational energies,  $E_t$ . Arrows point to the corresponding minimum for each curve. The curves were obtained by replotting the experimental data of Gostein and Sitz (Table II of [39]). The statistical uncertainties for the sticking probabilities were omitted in the figure for clarity. The corresponding incidence energies  $E_t$ , and the location of the minimum for each curve,  $j_{min}$ , are as follows:

 $\Box: E_t = 55 \pm 2 \text{ meV}, \ j_{min} = 4; \ \diamond: E_t = 73 \pm 3 \text{ meV}, \ j_{min} = 3; \ \bigcirc: E_t = 94 \pm 5 \text{ meV}, \ j_{min} = 1.$ 

Sitz for the sticking coefficients of  $H_2/Pd(111)$  (Fig. 5.1) are the shifts in the sticking probability curve minima when the incidence energy of  $H_2$  is varied. This, in turn, reminds us of our prediction for the hydrogen on Cu(111) system regarding the shifts in the sticking probability curve minima when the incidence energy is varied (§3.1.2 and [85]). This stresses the general importance of the incidence energy (velocity) of the impinging hydrogen molecule. Furthermore, we will also show here that considerable isotope effects should be observed for the j-dependence of the adsorption probability of hydrogen on Pd.

To account for the nonmonotonic dependence of the sticking probability of  $H_2$ on Pd(111) on the initial rotational state j of the impinging  $H_2$  molecule, and to show the significance of the incidence energy  $E_t$  in accounting for this interesting behavior, we considered the reaction of a  $H_2$  molecule impinging a *flat* Pd surface at normal incidence [36,82,85]. We did quantum mechanical calculations of the sticking probability by solving the time-independent Schrödinger equation for a  $H_2$ molecule moving under the influence of an orientation-dependent PES corresponding to the  $H_2/Pd$ -system [91,92] using the coupled-channel method [33,34] and the concept of a local reflection matrix [79]. The dynamical variables we have considered are the center-of-mass distance of the molecule from the surface, Z, and the polar and azimuthal angular orientation of the molecule with respect to the surface,  $\theta$ and  $\varphi$ , respectively. Our orientationally anisotropic, vibrationally adiabatic, model potential is based on qualitative features of available PES plots for  $H_2/Pd$ -surface





Figure 5.2. A molecular orientation dependent activation barrier  $V(s, \theta)$  ( $E_a = -0.35 \text{ eV}$ ,  $V_1 = 0.8 \text{ eV}$ ,  $\beta = 0.25$ , and in this figure  $\alpha = 1.0 \text{ Å}^{-1}$ ). The +s-region corresponds to the surface side. The upper figure shows how the activation barrier changes with the molecular orientation. Notice the corresponding attractive well for a parallel ( $\theta = \pi/2$ ) orientation. From [36].

system [91,92] (cf., Fig. 5.2). The energy barrier for a perpendicular-oriented H<sub>2</sub> molecule was set at  $V_{max} = V_{\perp} \approx 0.80$  eV, and gradually decreased to a value  $V_{min} = V_{\parallel} \approx -0.35$  eV (an *attractive* potential) for a parallel-oriented molecule. The final sticking probability data result from a sum over *all* the contributions from *all* possible types of rotation (helicopter-type—with the rotational axis of the molecule oriented predominantly prependicular to the surface, cartwheel-type—with the rotational axis of the molecule oriented predominantly prependicular to the surface, cartwheel-type—with the rotation with the rotational axis oriented intermediate between the two former ones). Please refer to Chapter 2 for more details regarding the calculation method, and the actual form of the model potential adopted.



Figure 5.3. Numerical results for the *j*-dependent sticking probability curves for H<sub>2</sub> on Pd(111) in the vibrational ground state and fixed incidence energies,  $E_t$ . Arrows point to the corresponding minimum for each curve. (H<sub>2</sub>/Pd(111):  $V_{max} = V_{\perp} \approx 0.80$  eV,  $V_{min} = V_{\parallel} \approx -0.35$  eV.) The corresponding incidence energies,  $E_t$ , and the location of the minimum for each curve,  $j_{min}$ , are as follows:  $\diamond: E_t = 45 \text{ meV}, j_{min} = 3$ ; filled  $\diamond: E_t = 55 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 2$ ; filled  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 2$ ; filled  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 2$ ; filled  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 2$ ; filled  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 2$ ; filled  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 2$ ; filled  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 75 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 3$ ;  $\Box: E_t = 30 \text{ meV}$ ;  $E_t = 30 \text{ meV}, j_{min} = 30 \text{ meV}$ 

### $j_{min} = 2$ ; $\Delta : E_t = 85 \text{ meV}, j_{min} = 2$ ; filled $\Delta : E_t = 350 \text{ meV}, j_{min} = 2$ .

#### 5.1.1 Steering and Energy Transfer Effects

In Fig. 5.3 we show the sticking probability results for  $H_2$ . Aside from the structure we see in the range  $3 \le j \le 5$ , which we will discuss later, we can also see that there is a good agreement with the experimental trend in that the sticking probability initially decreases with increasing initial rotational state  $(j = 0 \rightarrow 3)$ , for low j, then increases again for higher j (j > 4). There is also a general shift of the sticking probability curve minimum towards lower j as the incidence energy increases. The discrepancy in magnitude between our results and that of the experiment is most likely due to our reduced dimensionality. Some sites along the Pd(111) surface have higher barriers to dissociation, or less attractive wells than the one we have considered here, which will then reduce the dissociation. Earlier studies concerning with the dissociation of H<sub>2</sub> on Cu [58,59,76,113], Pd(100) [76,91,92,114], W(100) [115], and Rh(100) [92,116,117] have shown the importance of surface corrugation, and for a perfect quantitative explanation of the process, a multi-dimensional description is, of course, required. However, we believe that our basic picture, in which, qualitatively, the nonmonotonic dependence of the sticking probability on the initial rotational state j of the impinging hydrogen molecule, and the strong dependence on its incidence energy are general features of an orientation dependent reaction, such as the dissociative adsorption of hydrogen on metal surfaces, will not change. Furthermore, we obtained the same general features for the j- and  $E_t$ -dependence

of the sticking probability of H<sub>2</sub> using other values for  $V_{max}$  and  $V_{min}$ .

When a hydrogen molecule approaches a metal surface, it encounters an orientation-dependent potential energy (hyper-) surface (PES) [58-60,91,92]. In order for the molecule to dissociate and be adsorbed on the surface, it must be able to find the *path of least resistance* (path of least potential), and have enough energy to reach the surface. This process depends on what the initial rotational- and vibrational-states of the impinging hydrogen molecule are, what its incidence energy is, and how long it stays under the influence of the anisotropic PES [36,82,85]. As mentioned earlier (Chapter 3), in the case of rotation, there are two competing factors working for the dissociation process, *viz., Steering* (dynamical reorientation) and *R-T* (rotational-translational) *energy transfer* (*via* bond-length extension). The first, *Steering*, which originates from the orientational dependence of the dissociative adsorption process, pertains to a dynamical reorientation of the impinging molecule towards a more favorable orientation (a predominantly parallel orientation). However, there are two ways by which *Steering* can reduce the adsorption probability-

- 1. by shortening the amount of time that the molecule spends in a favorable orientation, or
- 2. by consuming some translational energy needed for dissociation, in an attempt to reorient molecules that approach the surface with an initially unfavorable orientation to a favorable one.

Steering dominates when the impinging molecule does not have sufficient rotational energy to assist in its adsorption. The second, R-T energy transfer, which originates from the strong coupling between the rotational and translational degrees-of-freedom, pertains to the effective transfer of rotational energy to translational energy. As the molecule approaches the surface, a considerable stretching of the molecular bond-length (Bond-Length Extension) occurs, which in turn increases the moment-of-inertia of the molecule. An increase in the moment-of-inertia leads to a corresponding decrease in the rotational constant and, in effect, the rotational energy. Thus, because of the strong coupling between the rotational and translational degrees-of-freedom, if there is no change in the rotational state of the impinging molecule, and the conservation of energy is to be satisfied, any decrease in the rotational energy due to Bond-Length Extension will be efficiently transferred to the translational energy and assist in the dissociation. R-T energy transfer dominates when the impinging hydrogen molecule has sufficient rotational energy to assist in its adsorption.

For low initial rotational states, because of the rather small rotational energy, Steering will be dominant. As the molecule approaches the surface, it is steered to different regions of the anisotropic PES. Whether it will reach a point of relatively low potential on time determines whether the molecule will be adsorbed.

For high initial rotational states, the molecule has sufficient rotational energy to assist in dissociation. Furthermore, to the surface the molecule becomes a blur. (In some sense, the surface cannot distinguish in which orientation the molecule is.) Thus, R-T energy transfer will be dominant.

The combined effect of these two factors leads to an initial decrease and then, eventually, an increase in the sticking probability as the initial rotational state of the impinging molecule is increased for a fixed incidence energy (cf., e.g., curve



Figure 5.4. Numerical results for the j-dependent sticking probability curves for D2 on Pd(111) in the vibrational ground state and fixed incidence energies,  $E_t$ . Arrows point to the corresponding minimum for each curve.  $(D_2/Pd(111): V_{max} = V_{\perp} \approx 0.80 \text{ eV}, V_{min} = V_{\parallel} \approx -0.35 \text{ eV}.)$  The corresponding incidence energies,  $E_t$ , and the horizontal production of the minimum for each curve. the location of the minimum for each curve,  $j_{min}$ , are as follows:  $\diamond: E_t = 45 \text{ meV}, j_{min} = 3$ ; filled  $\diamond: E_t = 55 \text{ meV}, j_{min} = 5$ ;  $\Box: E_t = 65 \text{ meV}, j_{min} = 5$ ; filled  $\Box: E_t = 75 \text{ meV}, j_{min} = 5$ ; filled  $\Box:$ 

 $j_{min} = 4$ ;  $\Delta: E_t = 85 \text{ meV}, j_{min} = 4$ ; filled  $\Delta: E_t = 350 \text{ meV}, j_{min} = 1$ .

corresponding to 55 meV in Figs. 5.1 & 5.3). Because any positive incidence energy given to the impinging hydrogen molecule will be greater than the minimum barrier, as the incidence energy is increased, even a slight contribution from the rotational energy will be sufficient to assist in dissociation. Thus, the efficacy of R-Tenergy transfer increases with increasing incidence energy and we see a corresponding shift in the curve minimum towards lower initial rotational states (cf., curves corresponding to 55 meV and 75 meV in Figs. 5.1 & 5.3).

#### 5.1.2Isotope Effects

In addition, we can also observe strong isotope effects when we compare our calculation results for the dissociation of  $H_2/Pd(111)$  (Fig. 5.3) with those for  $D_2/Pd(111)$ (Fig. 5.4). For the same incidence energy  $E_t$ , we can immediately see that the locations of the minima for the sticking probability curves of  $D_2$  are shifted more towards higher rotational states  $(j = 5 \rightarrow 8)$  (Fig. 5.4) as compared to those of H<sub>2</sub>  $(j = 4 \rightarrow 5)$  (Fig. 5.3), with the H<sub>2</sub> molecules exhibiting higher sticking probabilities than  $D_2$  molecules in the high j region. Because a  $D_2$  molecule is much slower than a H<sub>2</sub> molecule, even for the same incidence energy  $E_t$ , Steering will be more effective with the  $D_2$  molecules than the  $H_2$  molecules. Furthermore, the  $D_2$  molecules have a lower rotational constant compared to  $H_2$  molecules, and we will need higher j



Figure 5.5. Rotational alignment for D<sub>2</sub> molecules desorbing in the state ( $\nu = 0, j, E_t$ ) from a Pd surface as a function of the final translational energy  $E_t$ . Final rotational state  $j = 8 \rightarrow 14$ . Surface temperature  $T_S = 690$  K.

states for  $D_2$  before the *R-T* energy transfer could dominate and for the sticking probability curve to increase again in the higher j region. Thus, we observe that the minima of the sticking probability curves for  $D_2$  molecules are shifted more towards higher j than those for  $H_2$  molecules.

With regard to the structure we see in Figs. 5.3 & 5.4, because of the structure of the PES we have adapted, some trapping process may occur where the molecules cannot escape and dissociate because of too much rotation, nor can they be reflected back because there is not enough translational energy (rotationally mediated selective adsorption). Because these resonances are quantized, the structures we see in Figs. 5.3 & 5.4 could occur if the total energy coincides with a resonance energy. As we can see, these structures disappear at high rotational states (j > 10) and high incidence energies  $(E_t = 300 \text{ meV})$ . We will present a more detailed discussion of these structures, and the isotope and surface temperature effects in the adsorption and desorption of hydrogen on palladium system in the near future.

# 5.2 Rotational Effects in the Associative Desorption Dynamics

#### 5.2.1 Rotational Alignment & Dynamical Quantum Filtering

As a rotational quantum state filter, how effective is the Pd surface compared to the Cu surface? To consider this, we again calculated for the alignment factors  $A_0^2(j)$
corresponding to each final rotational state j a D<sub>2</sub> molecule assumes after desorbing from a Pd surface. (The calculation method is as described in Chapter 2 and  $\S4.2$ .) In Fig. 5.5 we show the calculated  $E_t$ -dependent alignment factor  $A_0^2(j)$  results for  $D_2$  molecules desorbing in the vibrational ground state ( $\nu = 0$ ) from a Pd surface, with final rotational states  $j = 8 \rightarrow 14$ . We see that unlike the desorption of D<sub>2</sub> from Cu(111) (cf., Fig. 4.5), there are no molecules doing cartwheel-like rotations. This is to be expected. At the final translational energies  $E_t$  considered in Fig. 5.5, the corresponding total kinetic energies  $E_{tot}$  are small, and the maximum final rotational states  $j_{max}$  accessible to the desorbing D<sub>2</sub> molecules are almost the same as the final rotational state j the desorbing D<sub>2</sub> molecules assume, i.e.,  $j \approx j_{max}$ . Because of the considerably small barrier minimum for the D<sub>2</sub>/Pd-surface system ( $V_{min} \approx$ -0.35 eV), the corresponding critical rotational states  $j_{crit}$  are approximately the same as the maximum final rotational state  $j_{max}$  accessible to the desorbing D<sub>2</sub> molecules, *i.e.*,  $j_{crit} \approx j_{max}$ . From arguments presented earlier in §4.2, the desorbing molecules are bound to follow the path of least resistance, which corresponds to an orientation parallel to the surface, and, as a result, the desorbing  $D_2$  molecules will show a helicopter-like rotational preference. Thus, to answer the question we have posed earlier in this section, with low energies  $(E_t < 0.25 \text{ eV})$ , as a filter, Pd surfaces are more effective in producing helicopter-like rotating  $D_2$  molecules, and Cu surfaces are more effective in producing cartwheel-like rotating  $D_2$  molecules (cf., Fig. 4.5).

## Chapter 6

# Summary, Conclusions, and Further Discussions

This thesis was based, in part, on earlier and ongoing studies [36, 40, 82–89] on orientational effects on the activated [36, 82–87] and the non-activated [40] dissociation of hydrogen molecules on metal surfaces, and the reverse process of association and then desorption from metal surfaces [83–89]. Throughout this study, we tried to answer the following general questions—What is the role of the molecular orientation on the dynamics of hydrogen-surface reactions? How can this be understood based on the model we have adopted? How can they be verified experimentally? How are they related to earlier experimental results? What further experiments do we need to perform? How feasible is the idea we have proposed and what immediate use do we have for them?

In Chapter 2, we gave a full description of the model adopted to study the dynamics of hydrogen on copper and palladium surfaces, and considered both a *rigid* and a *dynamic* surface. We did quantum mechanical model calculations using the coupled-channel method [33,64] and the concept of a local reflection matrix [79]. Our model potential is based on qualitative features of available PES plots for the  $H_2/Cu$  surface [36,57-61] (*e.g.*, ab-initio PES calculation results of [57] shown in Fig. 2.3) and  $H_2/Pd$  surface [91,92] systems. We took advantage of the convenience gained in using the concept of a reaction path (*cf.*, *e.g.*, [64]).

In Chapter 3, we gave a full discussion of our results concerning the rotational effects on the dissociative adsorption dynamics and inelastic scattering dynamics of  $H_2(D_2)$  on Cu(111). Our theoretical studies on the influence of molecular orientation on the dynamics of  $H_2(D_2)/Cu(111)$ , a paradigm of an *activated system*, show very interesting, surprising and general results.

For a rigid surface, we [36,40] showed that due to the inherent strong orientational dependence of hydrogen-solid surface reactions and the coupling between the different degrees of freedom involved, two competing factors working for the dissociative adsorption process, viz., Steering or the DYNAMICAL REORIENTATION factor and Rotational-Translational Energy Transfer or the ROTATIONAL ASSISTANCE via BOND-LENGTH EXTENSION factor, come into effect [36]. Furthermore, we showed that the Steering Effect, which is due to the anisotropic nature of the PES, dominates over the Energy Transfer Effect for low initial rotational states j. For high j, the Energy Transfer Effect, which arises from the strong coupling between the rotational motion and the motion along the reaction path, dominates. We also showed that the efficacy of these two factors is strongly dependent on the incidence translational energy of the impinging hydrogen molecule [85]. For molecules with incidence translational energies that are less than the activation barrier minimum  $V_{min}$ , corresponding to a favorable (parallel) orientation, Steering will not be sufficient in aiding the impinging molecule to dissociatively adsorb on the surface. Thus, Energy Transfer Effect will be dominant when the incidence translational energy is less than the activation barrier minimum. As a consequence, for a fixed incidence translational energy, the dissociative adsorption probability monotonically increases with increasing initial rotational states of the impinging molecule. As the incidence translational energy increases, the efficacy of *Steering* begins to increase and, for fixed incidence translational energies, we begin to observe a nonmonotonic dependence of the dissociative adsorption probability on the initial rotational state of the impinging molecule. When the incidence translational energy of the molecule is comparable with the barrier maximum, corresponding to an unfavorable (perpendicular) orientation, the molecule will already be travelling at such a high speed that there won't be enough time for the molecule to reorient. As a result, Steering again loses its efficacy, and we observe a monotonic increase in the dissociative adsorption probability as a function of the initial rotational state of the impinging molecule. The two competing factors mentioned above seem to be general features of orientation dependent processes, as they were later directly observed for the  $H_2/Pd(111)$  system [39], which, apart from exhibiting a strong orientation dependence, is described by a totally different PES, as we have discussed in detail in Chapter 5.

For a dynamic surface, where the surface lattice was modeled as independent Einstein oscillators, we showed that, in addition to the two factors mentioned above (Steering and Rotational-Translational Energy Transfer), we have the Recoil Effect. As a result of this Recoil Effect, the incidence translational energy dependent dissociative adsorption probability shows a slight increase in magnitude with increasing surface temperatures for low incidence translational energies (*i.e.*,  $E_t < V_{min}$ ), and a slight decrease in magnitude with increasing surface temperatures for high incidence translational energies (*i.e.*,  $E_t > V_{min}$ ).

In Chapter 4, we gave a corresponding full discussion concerning the rotational effects on the associative desorption dynamics of  $H_2(D_2)$  on Cu(111). We were able to consistently relate the calculated adsorption results with the desorption results [85] and, for the first time, reproduce the experimentally observed initial cooling, then a mild heating, followed by a cooling again of the rotational temperature of the desorbing hydrogen molecules with respect to the surface temperature. We were also able to explain the experimentally observed suprisingly low rotational alignment [41,47,50]. Furthermore, we suggested another means by which we could estimate the effective activation barrier experimentally, *i.e.*, by measuring the rotational alignment for different final total kinetic energies and determining the critical rotational states  $j_{crit}$  (cf., e.g., Table 4.1), indicated by the peaks appearing in Fig. 4.3. We also suggested a means by which we could produce oriented hydrogen molecules via the so-called Dynamical Quantum Filtering Effect [88,89], which takes advantage of the inherent nature of the desorption process to be orientation dependent. A comparison of the alignment results for  $D_2$  molecules desorbing from Cu and Pd surfaces at low energies indicates that the Cu surface is effective for producing cartwheeling D<sub>2</sub> molecules, and the Pd surface is effective for producing helicoptering  $D_2$  molecules.

In Chapter 5, we considered the rotational effects on the dynamics of  $H_2(D_2)$  on Pd(111), an example of a non-activated system. We showed that the experimental observations for the dissociative adsorption and associative desorption dynamics of  $H_2$  on Pd(111) could also be explained by considering the three factors mentioned above, indicating that Steering, Energy Transfer, and Dynamical Quantum Filtering are general, dynamical features of orientation dependent reactions [40].

So what is next? Although we are able to successfully account for various experimental trends that have so far been made, and also suggested some new experiments which might further our understanding of hydrogen-solid surface interaction, our task is far from complete. In fact, it would not be an exaggeration to say that the understanding of surface dynamics is far from complete [102]. On the contrary, it can be said that we have just begun. So far our study concerning the hydrogensolid surface reaction concentrated on the effects of the molecular orientation of the impinging and/or desorbing hydrogen molecules, and although it has so far been fairly accurate in explaining recent experimental observations, a fully quantitative agreement between current experimental results and available theoretical results has not yet been achieved. To do so would require an extension of the current fully quantum mechanical dynamical calculation to take into consideration higher dimensions, and eventually all the degrees of freedom of the impinging/desorbing hydrogen molecules and that of the surface atoms would have to be considered. Furthermore, there is also a need for more *ab-initio* calculations that would provide further information regarding the effective multi-dimensional potential energy surface governing the hydrogen-solid surface reaction. We propose-

- 1. to consider the feasibility of extending our current fully quantum mechanical calculation to higher dimensions;
- 2. to study how the other degrees of freedom influence the hydrogen-solid surface reaction;
- 3. to study how we could verify/utilize/further our current knowledge regarding the hydrogen-solid surface reaction by proposing/suggesting new experiments and methods;
- 4. to consider the efficacy of semi-empirical model potentials as compared to interpolation by some functional form to match results of ab-initio calculations.

From these further studies—We expect to be able to extend our current fully quantum dynamical calculations to higher dimensions, which, eventually, would have to include all the 6 degrees of freedom of the impinging/desorbing hydrogen molecule and surface vibrations. This achievement in itself would pave the way for a more thorough understanding of hydrogen-solid surface reactions, with direct quantitative comparison with current and future experimental results involving state-specific reactions becoming possible.

However, regardless of how successful we are in including all degrees of freedom in our calculation, as mentioned above, from physical considerations, we could consider any pair, trio, or other combinations of the above mentioned degrees of freedom dynamically and freeze the others, in which case we expect that we will be able—

1. to clarify how the coupling between the different degrees of freedom influences the hydrogen-solid surface reaction;

- 2. to identify how the total energy may be effectively distributed among the different possible motions of the impinging/desorbing hydrogen molecule;
- 3. to identify the efficacy of introducing a limited amount of energy to any particular degree of freedom to promote or hinder the reaction between hydrogen molecules and solid surfaces;
- 4. to propose (suggest) new experiments and methods to verify, utilize, and further our current knowledge regarding the hydrogen-solid surface reaction;
- 5. to propose a general model potential that could be easily adapted to different hydrogen-solid surface systems with barrier heights that could be chosen to match those obtained in ab-initio calculations;
- 6. to extend our current study to more catalytically interesting systems such as those involving alloys, and utilize our current knowledge to introduce novel materials and novel means of taking advantage of the inherent nature of the reactions we have studied, that would not only benefit us academically and industrially, but would also be environment friendly.

Thus, from these and further studies, we expect to be able to make significant contributions, not only in attaining a fundamental understanding of different surface reactions, but also in the technological development of novel materials, that are not only user-friendly, but are also environment-friendly. Recently, several researchers are proposing ingenious techniques [118–121] to apply combinatorial chemistry the shotgun approach to chemical discovery, developed and applied extensively by the pharmaceutical industry, whereby researchers synthesize and test hundreds or thousands of compounds simultaneously [118,119]—to find hot novel materials, such as catalysts and superconductors. Although these techniques may succeed in finding new materials that are more efficient than those in commercial use now, the materials found may not always turn out to be ideal, neither user-wise nor environment-wise. On the other hand, it would not be good business strategy to invest precious funds and not use these materials, just because they involve toxic materials.

What would be more desirable is a systematic theoretical study of the differences in reactivities between different classes of molecules with a surface, and the differences in reactivities between different surfaces with a class of molecules. Insights into the structure of surfaces combined with an understanding of the relation between the surface composition and reactivity could then lead to new ideas for ideal novel materials design. Only then should synthesis, characterization, and test be performed. However, if ever we are to attain a real understanding of why there is an enormous difference in reactivity of different classes of molecules with a surface, and also a great difference in reactivity of different surfaces with a class of molecules, we must know the elementary steps involved in the reactions concerned, and the identity of the rate-limiting reaction intermediate. Only then, with this knowledge, can we proceed to determine the structure of this reaction complex and relate its reactivity to the electronic nature of the reaction complex through theory.

### References

- [1] P.J. Feibelman and J. Harris, Nature 372 (1994) 135.
- [2] B. Cagnac, M.D. Plimmer, L. Julien, and F. Biraben, Rep. Prog. Phys. 57 (1994) 853.
- [3] Y. Fukai, The Metal-Hydrogen System (Springer-Verlag, Berlin, 1993).
- [4] B.M. Andreev, E.P. Magomedbekov, and G.H. Sicking, Interaction of Hydrogen Isotopes with Transition Metals and Intermetallic Compounds (Springer-Verlag, Berlin, 1996).
- [5] H. Wipf, Hydrogen in Metals III (Springer-Verlag, Berlin, 1997).
- [6] M.S. Daw and M.I. Baskes, *Phys. Rev. Lett.* **50** (1983) 1285.
- [7] H. Vehoff, Topics in Applied Physics 73, ed. H. Wipf (Springer-Verlag, Berlin, 1997) p. 215.
- [8] D.P. Gregory, Sci. Am. 228 (January 1973) 13.
- [9] P. Dantzer, *Topics in Applied Physics* 73, ed. H. Wipf (Springer-Verlag, Berlin, 1997) p. 279.
- [10] H.A. Michelsen, C.T. Rettner, and D.J. Auerbach, Springer Series in Surface Science 34, ed. R.J. Madix (Springer-Verlag, Berlin, 1994) p. 185.
- [11] K.D. Rendulic and A. Winkler, Surf. Sci. 299/300 (1994) 261.
- [12] S. Holloway, Surf. Sci. 299/300 (1994) 656.
- [13] W. van Willigen, Phys. Lett. A28 (1968) 80.
- [14] M. Balooch, M.J. Cardillo, D.R. Miller, and R.E. Stickney, Surf. Sci. 46 (1974) 358.
- [15] M. Balooch, M.J. Cardillo, and R.E. Stickney, Surf. Sci. 50 (1975) 263.
- [16] M. Grueble and A.H. Zewail, *Physics Today* 43 (May 1990) 24.
- [17] R.B. Bernstein, Chemical Dynamics via Molecular Beam and Laser Techniques (Oxford University, New York, 1982).
- [18] R.D. Levine and R.B. Bernstein, Molecular Dynamics and Chemical Reactivity (Oxford University, New York, 1987).

- [19] G. Ehrlich, Chemistry and Physics of Solid Surfaces 7, eds. R. Vanselow and R. Howe (Springer-Verlag, Berlin, 1988).
- [20] C.T. Rettner and M.N.R. Ashfold, *Dynamics of Gas-Surface Collisions* (Royal Society of Chemistry, Cambridge, 1991).
- [21] S. Holloway, Dynamics of Gas-Surface Collisions, eds. C.T. Rettner and M.N.R. Ashfold (Royal Society of Chemistry, Cambridge, 1991).
- [22] B.E. Hayden, Dynamics of Gas-Surface Collisions, eds. C.T. Rettner and M.N.R. Ashfold (Royal Society of Chemistry, Cambridge, 1991).
- [23] G.R. Darling and S. Holloway, Rep. Prog. Phys. 58 (1995) 1595.
- [24] C.T. Rettner, D.J. Auerbach, and H.A. Michelsen, Phys. Rev. Lett. 68 (1992) 1164.
- [25] H.A. Michelsen, C.T. Rettner, and D.J. Auerbach, Surf. Sci. 272 (1992) 65.
- [26] J.-H. Rechtien, R. Harder, G. Herrmann, and K.J. Snowdon, Surf. Sci. 272 (1992) 240.
- [27] U. Heinzmann, S. Holloway, A.W. Kleyn, R.E. Palmer, and K.J. Snowdon, J. Phys.: Condens. Matter 8 (1996) 3245.
- [28] G.D. Kubiak, G.O. Sitz, and R.N. Zare, J. Chem. Phys. 81 (1984) 6397; 83 (1985) 2538.
- [29] L. Schröter, R. David, and H. Zacharias, Surf. Sci. 258 (1991) 259.
- [30] H.A. Michelsen, C.T. Rettner, and D.J. Auerbach, Phys. Rev. Lett. 69 (1992) 2678.
- [31] H.A. Michelsen, C.T. Rettner, D.J. Auerbach, and R.N. Zare, J. Chem. Phys. 98 (1993) 8294.
- [32] C.T. Rettner, H.A. Michelsen, and D.J. Auerbach, J. Chem. Phys. 102 (1995) 4625.
- [33] H. Kasai and A. Okiji, Prog. Theor. Phys. Suppl. 106 (1991) 341.
- [34] H. Kasai and A. Okiji, Prog. Surf. Sci. 44 (1993) 101.
- [35] We will be using the terms adsorption, dissociation, and sticking interchangeably to refer to the dissociation of hydrogen molecules into hydrogen atoms that are then adsorbed on the Cu surface.
- [36] W.A. Diño, H. Kasai, and A. Okiji, J. Phys. Soc. Jpn. 64 (1995) 2478.
- [37] C.T. Rettner and D.J. Auerbach, Chem. Phys. Lett. 253 (1996) 236.
- [38] M. Beautl, M. Riedler, and K.D. Rendulic, Chem. Phys. Lett. 256 (1996) 33.
- [39] M. Gostein and G.O. Sitz, J. Chem. Phys. 106 (1997) 7378.

- [40] W.A. Diño, H. Kasai, and A. Okiji, J. Phys. Soc. Jpn. 66 (1997) 3344.
- [41] D. Wetzig, R. Dopheide, M. Rutkowski, R. David, and H. Zacharias, Phys. Rev. Lett. 76 (1995) 463.
- [42] U. Fano and J.H. Macek, Rev. Mod. Phys. 54 (1973) 553.
- [43] C.H. Greene and R.N. Zare, Ann. Rev. Phys. Chem. 33 (1982) 119.
- [44] C.H. Greene and R.N. Zare, J. Chem. Phys. 78 (1983) 6741.
- [45] R.N. Zare, Angular Momentum (Wiley, New York, 1988).
- [46] D. Wetzig, M. Rutkowski, W. Etterich, R. David, and H. Zacharias, Surf. Sci. 402-404 (1998) 232.
- [47] D. Wetzig, M. Rutkowski, R. David, and H. Zacharias, Europhys. Lett. 36 (1996) 31.
- [48] E.E. Marinero, C.T. Rettner, and R.N. Zare, Phys. Rev. Lett. 19 (1982) 1323.
- [49] S.L. Anderson, G.D. Kubiak, and R.N. Zare, Chem. Phys. Lett. 105 (1984) 22.
- [50] S.J. Gulding, A.M. Wodtke, H. Hou, C.T. Rettner, H.A. Michelsen, and D.J. Auerbach, J. Chem. Phys. 105 (1996) 9702.
- [51] P.K. Johansson, Surf. Sci. 104 (1981) 510.
- [52] A. Okiji, H. Kasai, and A. Kato, J. Phys. Soc. Jpn. 51 (1982) 3291.
- [53] P. Madhaven and J.L. Whitten, J. Chem. Phys. 77 (1982) 2673.
- [54] J. Harris and S. Andersson, Phys. Rev. Lett. 55 (1985) 1583.
- [55] C. Engdahl, B.I. Lundqvist, U. Nielsen, and J.K. Nørskov, Phys. Rev. B45 (1992) 11362.
- [56] J.E. Müller, Appl. Phys. A49 (1989) 681; Surf. Sci. 272 (1992) 45.
- [57] K. Tanada, Masterral Thesis, Faculty of Engineering, Osaka University, Japan (1993).
- [58] B. Hammer, M. Scheffler, K.W. Jacobsen, and J.K. Nørskov, *Phys. Rev. Lett.* 73 (1994) 1400.
- [59] J.A. White and D.M. Bird, Chem. Phys. Lett. 213 (1993) 422; J.A. White,
  D.M. Bird, M.C. Payne, and I. Stich, Phys. Rev. Lett. 73 (1994) 1404.
- [60] P. Kratzer, B. Hammer, and J.K. Nørskov, Surf. Sci. 359 (1996) 45.
- [61] G. Wiesenekker, G.J. Kroes, and E.J. Baerends, J. Chem. Phys. 104 (1996) 7344.

- [62] A. Hanbicki and E.W. Plummer, Proceedings of the Oji Seminar on "Chemical Processes at Surfaces based on Atomic Scale Structure and Dynamics", ed. K. Tanaka (WORDS Publishing House, Tokyo, 1996) p. 1.
- [63] M.R. Hand and S. Holloway, J. Chem. Phys. 91 (1989) 7209.
- [64] W. Brenig and H. Kasai, Surf. Sci. 213 (1989) 170.
- [65] J. Harris, Surf. Sci. 221 (1989) 335.
- [66] D. Halstead and S. Holloway, J. Chem. Phys. 93 (1990) 2859.
- [67] A. Okiji and H. Kasai, Springer Series in Materials Science 17, eds. A. Yoshimori, T. Shinjo, and H. Watanabe (Springer-Verlag, Berlin, 1992) p. 253.
- [68] A. Gelb and M. Cardillo, Surf. Sci. 59 (1976) 128.
- [69] C.Y. Lee and A.E. DePristo, J. Chem. Phys. 87 (1987) 1401.
- [70] A. Kara and A.E. DePristo, J. Chem. Phys. 88 (1988) 5240.
- [71] S. Holloway, J. Phys.: Condens. Matter 3 (1991) S43.
- [72] J. Sheng and J.Z.H. Zhang, J. Chem. Phys. 97 (1992) 6784.
- [73] G.R. Darling and S. Holloway, J. Chem. Phys. 101 (1994) 3268.
- [74] T. Brunner and W. Brenig, Surf. Sci. 317 (1994) 303.
- [75] A. Gross, B. Hammer, M. Scheffler, and W. Brenig, *Phys. Rev. Lett.* 73 (1994) 3121.
- [76] A. Gross, J. Chem. Phys. 102 (1995) 5045.
- [77] A. Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. 75 (1995) 2718.
- [78] J. Dai and J. C. Light, J. Chem. Phys. 107 (1997) 1676.
- [79] W. Brenig, T. Brunner, A. Groß, and R. Russ, Z. Phys. B93 (1993) 91.
- [80] H. Kasai and A. Okiji, Surf. Sci. 242 (1991) 394.
- [81] L.D. Landau and E.M. Lifshitz, Quantum Mechanics, 3rd ed. (Pergamon Press Ltd., Oxford, 1977) §25, Problem 4.
- [82] W.A. Diño, H. Kasai, and A. Okiji, Surf. Sci. 363 (1996) 52.
- [83] H. Kasai, W.A. Diño, and A. Okiji, Springer Series in Solid-State Science 121, eds. A. Okiji, H. Kasai, and K. Makoshi (Springer-Verlag, Berlin, 1996) p. 99.
- [84] H. Kasai, W.A. Diño, and A. Okiji, Chemical Processes at Surfaces based on Atomic Scale Structures and Dynamics, ed. K. Tanaka (WORDS Publishing House, Tokyo, 1996) p. 223.
- [85] W.A. Diño, H. Kasai, and A. Okiji, Phys. Rev. Lett. 78 (1997) 286.

- [86] H. Kasai, W.A. Diño, and A. Okiji, Butsuri 52 (1997) 824 (in Japanese).
- [87] A. Okiji, H. Kasai, and W.A. Diño, Current Problems in Condensed Matter: Theory and Experiments, ed. J.L. Moran-Lopez (Plenum Press, N.Y., 1998) 275-282.
- [88] W.A. Diño, H. Kasai, and A. Okiji, J. Phys. Soc. Jpn. 67 (1998) 1517.
- [89] W.A. Diño, H. Kasai, and A. Okiji, Surf. Sci. 418 (1998) L39.
- [90] W.A. Diño, H. Kasai, and A. Okiji, Surf. Sci. (to be published).
- [91] S. Wilke and M. Scheffler, *Phys. Rev.* B53 (1996) 4926.
- [92] A. Eichler, G. Kreese, and J. Hafner, Surf. Sci. 397 (1998) 116.
- [93] S. Goldstone, K.J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., N.Y., 1941).
- [94] R.A. Marcus, J. Chem. Phys. 41 (1964) 603, 610, 2614.
- [95] R.A. Marcus, J. Chem. Phys. 45 (1966) 4493, 4500.
- [96] C.C. Rankin and J.C. Light, J. Chem. Phys. 51 (1969) 1701.
- [97] G. Miller and J.C. Light, J. Chem. Phys. 54 (1971) 1635, 1643.
- [98] We will be using the term molecule here to refer to a homonuclear diatomic molecule like  $H_2$  and  $D_2$ .
- [99] H. Hou, S.J. Gulding, C.T. Rettner, A.M. Wodtke, and D.J. Auerbach, Science 277 (1997) 80.
- [100] H. Zacharias, private communications.
- [101] D.J. Auerbach, private communications.
- [102] R.J. Madix, Springer Series in Surface Science 34, ed. R.J. Madix (Springer-Verlag, Berlin, 1994) p. 1.
- [103] A. Groß, Surf. Sci. 314 (1994) L843; 320 (1994) L68.
- [104] G.R. Darling and S. Holloway, Surf. Sci. 321 (1994) L189.
- [105] H.A. Michelsen and D.J. Auerbach, J. Chem. Phys. 94 (1991) 7502.
- [106] C. Engdahl and B.I. Lundqvist, Chem. Phys. Lett. 215 (1993) 103.
- [107] D.J. Auerbach, C.T. Rettner, and H.A. Michelsen, Surf. Sci. 283 (1993) 1.
- [108] M.R. Hand and J. Harris, J. Chem. Phys. 92 (1990) 7610.
- [109] W. Brenig, H. Kasai, and H. Müller, Surf. Sci. 161 (1985) 608.

- [110] W. Brenig, H. Kasai, and H. Müller, Springer Series in Solid-State Physics 50, eds. A. Yoshimori and M. Tsukada (Springer-Verlag, Berlin, 1985) p. 2.
- [111] J. Harris, J. Simon, A.C. Luntz, C.B. Mullins, and C.T. Rettner, Phys. Rev. Lett. 67 (1991) 652.
- [112] A.C. Luntz and J. Harris, Surf. Sci. 258 (1991) 397.
- [113] J. Dai and J.Z.H. Zhang, J. Chem. Phys. 102 (1995) 6280.
- [114] A. Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. 75 (1995) 2718.
- [115] M. Kay, G.R. Darling, S. Holloway, J.A. White, and D.M. Bird, Chem. Phys. Lett. 245 (1995) 311.
- [116] P.J. Feibelman, Phys. Rev. Lett. 67 (1991) 461.
- [117] A. Eichler, G. Kresse, and J. Hafner, Phys. Rev. Lett. 77 (1996) 1119.
- [118] R.F. Service, Science 280 (1998) 1690.
- [119] I.E. Maxwell, Nature 394 (1998) 325.
- [120] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, and T.E. Mallouk, *Science* 280 (1998) 1735.
- [121] S.M. Senkan, Nature 394 (1998) 350.

### Acknowledgements

In preparing and writing this thesis, many people have given me their help, encouragement, advice, and their never ending patience. Without them I could never, ever, have done this.

To my supervisor Professor Hideaki Kasai, thank you very much for your advice and help with regard to my daily life in Japan, and also with regard to my studies. Thank you very much for taking me under your direct supervision and introducing me to the world of Surface Science. And to your wife and children, thank you very much for being such wonderful and gracious hosts during my visits to your house.

To Professor Emeritus Ayao Okiji, thank you very much for your advice and help, not only with regard to my studies, by also with regard to my daily life here in Japan. Thank you very much for your comments and brilliant insights, opening my eyes to new avenues and new ways of looking at physics and life.

To Professor Norio Kawakami, Assistant Professor Seiichiro Suga, and Research Associates Dr. Hiroshi Nakanishi and Dr. Seiya Kumada, thank you very much for your hospitality and understanding, as well as for the constructive criticisms, comments and insights you have provided that had made this work possible.

To Dr. Hiroshi Nakanishi, again, thank you very much for your time and assistance in managing the computers I used to do the calculations presented in this thesis.

To Professors Hideaki Kasai, Norio Kawakami, Hiroshi Iwasaki, Kazuyoshi Itoh, and Assistant Professor Young-Whoan Beag, thank you very much for the precious time and kind considerations you extended to me in reading this manuscript, and for the helpful comments and constructive criticisms.

To Mses. Nobuko Yokoyama, Kyoko Nakamura, and Naoko Tani, thank you very much for your help with regard to administrative matters. But most of all, thank you very much for your radiant smiles that greet me everyday when I come to the Lab. Your smiles always brighten my day. Thank you very much for the daily morale boosts.

To the students of the Okiji Research Lab and the students (past and present) of the Kasai Research Lab, thank you very much for the warm atmosphere of camaraderie that your presence creates in the Lab, and for tolerating my company. Thank you for initiating conversations with me and entertaining my inane questions, my poor command of Nihongo notwithstanding. Thank you very much for showing me a side of Japan only a co-student could share.

To Professor Wilhelm Brenig and Dr. Yoshie Chiba-Kohno, thank you very much for your helpful comments and insights during the early stages of this work.

To Professors Yoshitada Murata, Tatsuo Okano, Katsuyuki Fukutani, and Dr. Maki Kawai, thank you very much for the warm hospitality and generosity you extended to me, when I visited your laboratories to learn more about the several exciting researches being done in your groups.

To the Ministry of Education, Science, Sports, and Culture (MONBUSHO) of Japan, and the Association of International Education, Japan (AIEJ), thank you very much for the financial support during my stay here in Japan.

To all my friends and acquaintances (Chinese, Filipino, Japanese, and other nationalities) within and outside the university, your kindness and warm hospitality has made me feel as if I have never left home, all through my stay (6 whole years!) here in Japan.

From the bottom of my heart—Thank you very much to you all!

And to my beloved family, thank you very much for your faith, support, encouragement, and understanding.

> Wilson Agerico Tan Diño 傅耀華 Osaka University 1998

#### List of Related Publications

- Wilson Agerico Diño, Hideaki Kasai, and Ayao Okiji, "Effects of Rotational State Excitations on the Dissociative Adsorption Dynamics of D<sub>2</sub>/Cu(111)" Journal of the Physical Society of Japan 64 (1995) 2478-2487.
- Wilson Agerico Diño, Hideaki Kasai, and Ayao Okiji, "Combined Effect of Molecular Rotational and Surface Vibrational Excitations on the Dissociative Adsorption of D<sub>2</sub>/Cu(111)" Surface Science 363 (1996) 52-61.
- Wilson Agerico Diño, Hideaki Kasai, and Ayao Okiji, "Role of Rotational Motion in the Dissociative Adsorption and Associative Desorption Dynamics of D<sub>2</sub>/Cu(111)" *Physical Review Letters* 78 (1997) 286-289.
- Wilson Agerico Diño, Hideaki Kasai, and Ayao Okiji, "Rotational Effects in the Dissociative Adsorption Dynamics of Hydrogen on a Pd Surface" Journal of the Physical Society of Japan 66 (1997) 3344-3347.
- Wilson Agerico Diño, Hideaki Kasai, and Ayao Okiji, "Rotational Alignment in the Associative Desorption Dynamics of Hydrogen Molecules from Metal Surfaces" Journal of the Physical Society of Japan 67 (1998) 1517-1520.
- Wilson Agerico Diño, Hideaki Kasai, and Ayao Okiji, "Dynamical Quantum Filtering in Hydrogen-Surface Reactions" Surface Science 418 (1998) L39-L44.
- Wilson Agerico Diño, Hideaki Kasai, and Ayao Okiji, "Rotational Polarization and Filtering of Hydrogen Molecules by Metal Surfaces—Isotope Effects" Surface Science, to be published.

#### Review

 8. 笠井秀明、Wilson Agerico Diño、興地斐男、 解離と会合一飛来する水素と離れ去る水素の金属表面での挙動ー 日本物理学会誌 52 (1997) 824-830.
 Hideaki Kasai, Wilson Agerico Diño, and Ayao Okiji, Dissociation and Association—Dynamical Behavior of Hydrogen Molecules Dissociatively Adsorbing on and/or Associatively Desorbing from Metal Surfaces Butsuri 52 (1997) 824-830.

#### Proceedings

- Hideaki Kasai, Ayao Okiji, and Wilson Agerico Diño, "On the Molecular Orientation Dependence of Dynamical Processes on Solid Surfaces: Dissociative Adsorption and Scattering" Springer Series in Solid-State Sciences 121, eds. A. Okiji, H. Kasai, and K. Makoshi (Springer-Verlag, Berlin, 1996) 99-111.
- Hideaki Kasai, Wilson Agerico Diño, and Ayao Okiji, "Molecular Orientation Dependence of Dynamical Processes at Metal Surfaces"

Proceedings of the Oji Seminar on "Chemical Processes at Surfaces based on Atomic Scale Structure and Dynamics", ed. K. Tanaka (WORDS Publishing House, Tokyo, 1996) 223-228.

11. Ayao Okiji, Hideaki Kasai, and Wilson Agerico Diño,

"Molecular Orientation Dependence of Dynamical Processes on Metal Surfaces: Dissociative Adsorption and Scattering, and Associative Desorption"

Proceedings of the International Workshop on the Current Problems in Condensed Matter: Theory and Experiment (Cocoyoc, Morelos, Mexico), ed. J.L. Moran-Lopez (Plenum Press, N.Y., 1998) 275-282.

