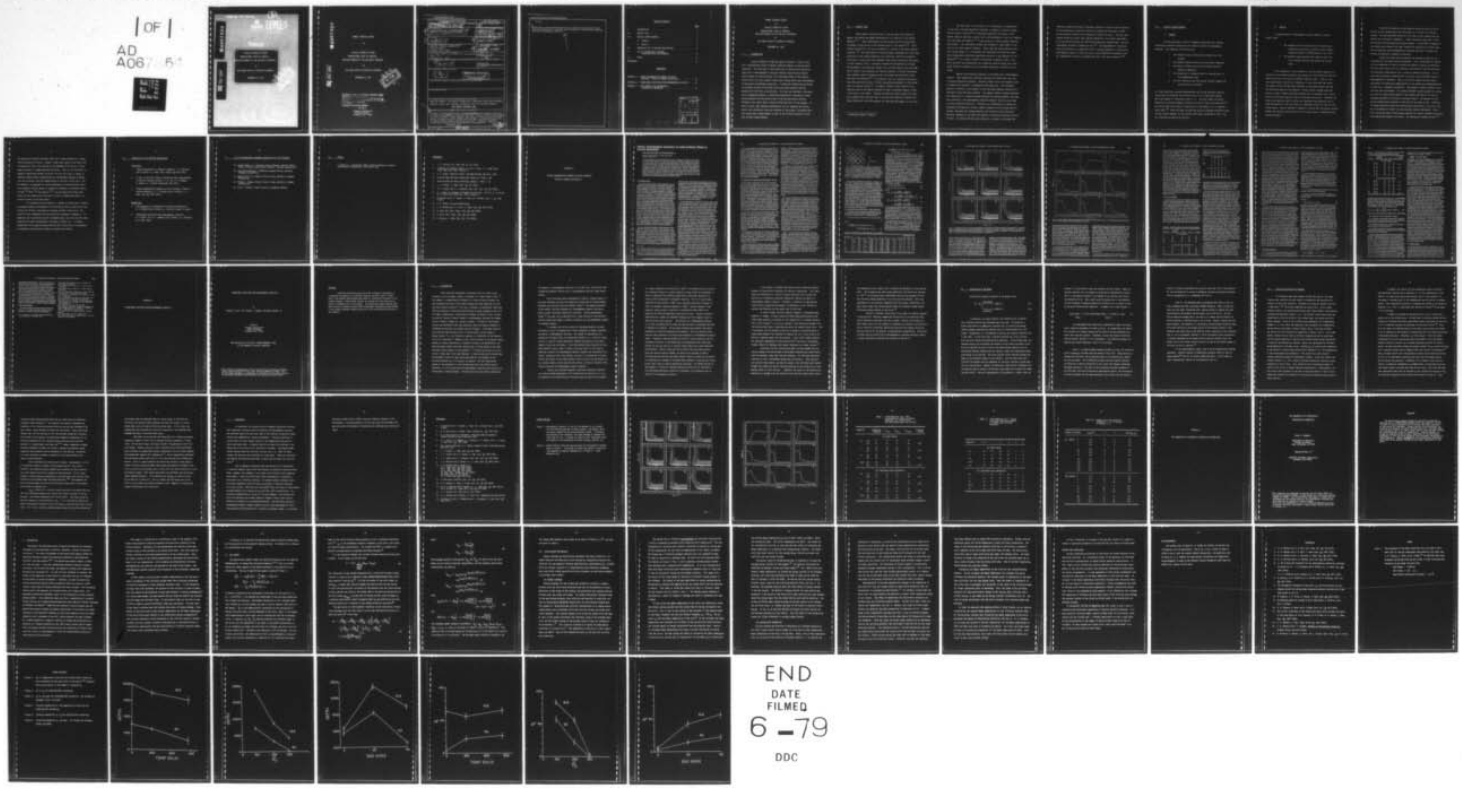
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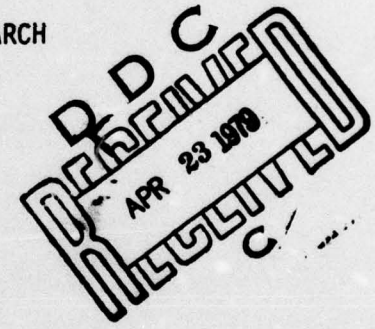
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By means of computer simulations, ~~we have determined~~ the necessary conditions for obtaining vibrational population inversions by means of reactions catalyzed by solid surfaces. A model potential describing in a realistic way the interactions of gases with solid surfaces was developed, including the possibility of energy transfer between the gas and the solid. Classical trajectory studies were carried out for both adsorption and desorption. A list of

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conditions has been produced detailing the conditions under which useful vibrational population inversions may be expected in the molecules produced from such heterogeneous catalysis.

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I. INTRODUCTION

Contract F49620-77-C-0004 was begun on October 1, 1976 to carry out a "Computational Study of Chemical Reaction Dynamics at the Gas-Solid Interface". The chief goal of the project was to ascertain the conditions under which a heterogeneously catalyzed chemical reaction would channel useful amounts of reaction energy into vibrational modes of the products. Possibilities for novel chemical lasers were forseen should such heterogeneous up-conversion be thoroughly understood. A three-year program was envisioned to elucidate by means of detailed calculations what features would be necessary for efficient up-conversions. This goal was realized in two years due to unexpected progress in developing computational procedures to model surface dynamics and the possibilities of gas-surface energy transfer. Therefore, this report marks a natural transition point in the program. In order to have a more coherent presentation, we will summarize our overall results and conclusions since the inception of the project, indicating separate second year accomplishments as part of the unified discussion of two-year program accomplishments.

II. PROJECT AIMS

When chemical reactions occur in the gas phase with release of energy, this energy may appear preferentially in vibration of the product molecule.[1]* These vibrationally excited product molecules may be used to produce lasing action in the infrared region of the spectrum.[2] Vibrationally excited HF or DF can be produced by a variety of gas phase chemical reactions.[3] The large amount of reaction energy, preference for vibrational excitation of the product molecules, and relatively inefficient quenching with typical diluent gases have produced large energy storage and high powers in DF/HF chemical lasers. Favorable transmission characteristics through the atmosphere, and relatively compact size, are two features that have made the DF chemical laser probably the leading candidate in the DoD high energy laser weapons program (although serious challenges from pulsed CO_2 lasers and others are emerging).[4] A DF chemical laser has reportedly destroyed a high speed antitank missile in flight, encouraging proponents of high energy lasers as weapons systems.[5] In summary, chemical lasers seem to be an important area of DoD concern expected to lead to prototype weapons systems in the early to mid 1980's. Research on molecular effects underlying chemically pumped lasers and novel ways to achieve such chemically pumped vibrational population inversions supports the long-term development of this area.

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* References appear on page 12.

One chief goal in this project is to investigate via computations a novel way to achieve population inversions in chemically reactive systems. The early work of Polanyi[6] on vibrational population inversions in exothermic chemical reactions in gases led to the development of the first chemical laser by Kasper and Pimental.[7] These systems all involve gaseous reactants and products. The intervening 18 years has witnessed a large growth in the field of gas phase chemical dynamics. Today, when gas phase molecules react and liberate energy, it is reasonably well understood the conditions under which considerable vibrational population inversion in the products will be obtained.[8] As a result, interest in obtaining "propensity rules", (e.g., which reactions have propensities for converting reaction energy into vibrational energy) has waned as far as gas phase bimolecular reactions are concerned.

However, much practical chemistry is performed with a heterogeneous catalyst. Many commercially desirable reactions are inefficient, too slow, or produce undesirable products. Carefully chosen solids are frequently used to promote such reactions in economically desirable ways. The automobile catalytic converter is one example in which gas phase chemical reactions are adjusted to yield desirable products. The present research program represents the second year of a research program designed to elucidate whether, and under what conditions, such heterogeneous catalyzed chemical reactions could lead to useful population inversion. Therefore, by a combination of theoretical techniques from materials science, chemical dynamics involving many-particle systems, semi-empirical quantum mechanics and non-equilibrium statistical mechanics (Appendix C), we model the dynamics of reactions occurring on solid surfaces. By analogy with gas phase chemistry, we expect to elucidate the

conditions under which useful vibrational population inversion may be obtained. As discussed below, we believe significant progress has been made in determining necessary conditions for population inversion to occur. The next step towards achieving a novel laser pumping mechanism is for careful experiments to be carried out testing and refining the hypothesis proposed here. One such experimental program is underway at Yale.[9] The measurement of vibrational state distributions for comparison with our current hypothesis is one way this experimental program is likely to evolve, having benefited considerably from our computational results as reported here and in the open literature.[10]

III. PROJECT ACCOMPLISHMENTS

A. Summary

We have performed a series of computer simulations that indicate vibrational excitation should occur for certain classes of heterogeneous reactions. The necessary restrictions are:

1. the reactants should dissociatively chemisorb on the surface
2. the product molecules should not dissociately chemisorb
3. the masses of atoms going into the product molecule should be comparable
4. the energy that is released should be released early in the recombination step
5. the solid should be such that energy transfer between the gas and solid is minimized.

For these conditions, we have estimated that ~67% of the available reaction energy could be channeled into vibration and, of this vibrational energy, about 60% appears in vibrational levels $V \geq 2$. The total amount of energy appearing as vibration compares favorably with the HF laser (also about 67%)[3] but the HF laser can be made to produce more of the energy in $V \geq 2$ (approximately 85%).[3] While our model calculations have not produced vibrational populations clearly superior to the existing (and highly optimized) HF laser, useful inversions do seem to be possible.

B. Details

A complete model of heterogeneous reaction dynamics involves several steps:

1. The reactants collide with the solid, dissociatively chemisorb and transfer a portion of their kinetic energy and energy of chemisorption to the solid;
2. The adsorbed atoms encounter each other on the solid, form a product molecule and emerge into the gas phase.

A key assumption in this research is that the energy appearing in vibration of the product molecules (and possibly as laser radiation) does not come from the solid but from the chemical reaction itself. That is, as a first approximation the solid is treated as a rigid substrate that alters the energy profile from gas phase reactants to gas phase products but does not contribute energy to the reaction. Energy transfer between gases and solids is often a rather inefficient process and, we speculate, not a likely source of sufficient energy to lead to vibrational excitation. Therefore, we look to the reaction itself to drive the vibrational up-conversion, and include the dynamics of the solid only as a secondary source (or sink) for the usable energy. Results reported in Appendix B confirm that the energy transfer between the reactants and the solid is not a major factor in determining the reaction dynamics.

Using this assumption, we performed an extensive series of calculations for the recombination step (#2 above) for a variety of different systems. This was performed during the first year of this research and the details are re-printed in Appendix A. These calculations used both a rigid surface and a surface permitting energy exchange. As described in Appendix A, the results were virtually the same; showing the possibility of useful population inversions from heterogeneously catalyzed reactions if certain conditions (as detailed in Appendix A) were met.

During the second year of research, the adsorption step (#1) was considered and two effects were investigated. First, the dynamics of adsorption was considered in order to estimate the amount of energy transferred to the solid (and, hence, lost to vibrational up-conversion) and the efficiency of dissociative chemisorption for a variety of potential surfaces. It was found that dissociative chemisorption is usually a very efficient process if thermodynamically favorable. That is, we did not observe serious kinetic bottlenecks to dissociative chemisorption if the process was thermodynamically allowed (e.g., exothermic adsorption). The process of energy transfer to the solid was more troublesome. All studies performed to date assumed the surface was rigid (a frozen lattice model) or the surface consisted of an array of uncoupled anharmonic oscillators (an Einstein model). We observed for the Einstein model energy transfers to the solid of the order of 10%. Therefore, it became important to make this estimate more accurate and, it was felt, the use of uncoupled oscillators was the area most needing improvement. Therefore, the second phase of the program undertook to replace uncoupled oscillators with generalized Langevin oscillators. As developed by Adelman and Doll[11]

the generalized Langevin equations (GLE) are a simple extension of a model using uncoupled oscillators. However, rather than using an oscillator with a conservative force, the coupling to the remainder of the solid is introduced by means of a damped Brownian oscillator. That is, the oscillator is damped to approximate energy dissipation into the solid and is subject to Brownian random forces to approximate the instantaneous pumping of energy into the oscillator from the random motions of the rest of the solid. The GLE method is an outgrowth of various techniques of non-equilibrium statistical mechanics and the theory of stochastic processes as developed chiefly by Kubo,[12] Mori,[13] and Zwanzig.[14] The GLE method has proved quite useful for gas-surface collisions and is likely to become more useful in a variety of areas in the near future.

In collaboration with Professor S. Adelman of Purdue and A. Diebold (a graduate student with Adelman), GLE calculations were carried out for comparison with Einstein calculations of energy transfer to the solid. The details of this computation and the results are reported in Appendix C. To summarize, GLE calculations predict increased energy loss into the solid when compared to Einstein calculations, by roughly a factor of 2. Therefore, perhaps 20% of the reaction energy could be lost to the solid in unfavorable circumstances and care must be taken to minimize this effect.

IV. CUMULATIVE LIST OF WRITTEN PUBLICATIONS

First Year

1. "Pattern Recognition in Chemical Dynamics", J. H. McCreery and G. Wolken, Jr., Chem. Phys. Letters 46, 469 (1977).

2. "A Test of the First Order Distorted Wave Born Approximation in Gas-Solid Energy Transfer", Y. W. Lin, S. A. Adelman, G. Wolken, Jr., Surface Science 66, 376 (1977).

3. "Atomic Recombination Dynamics on Solid Surfaces: Effects of Various Potentials", J. H. McCreery and G. Wolken, Jr., J. Chem. Phys. 67, 2551 (1977).

Second Year

1. "The Energetics of Diatom/Solid Dissociative Adsorption", A. C. Diebold and G. Wolken, Jr., Surface Science (in press).

2. "Vibrational Excitation From Heterogeneous Catalysis", G. D. Purvis III, M. J. Redmon, and G. Wolken, Jr., submitted to J. Phys. Chem.

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Dr. Jane Hylton McCreery, Information Systems Section, Battelle, Columbus Laboratories.

Dr. George Purvis III, Chemical Physics Group, Battelle, Columbus Laboratories.

Dr. Michael J. Redmon, Chemical Physics Group, Battelle, Columbus Laboratories.

Mr. Alain C. Diebold, Purdue University (graduate student).

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APPENDIX A

"ATOMIC RECOMBINATION DYNAMICS ON SOLID SURFACES: EFFECT OF VARIOUS POTENTIALS"

Atomic recombination dynamics on solid surfaces: Effect of various potentials[a)]

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(Received 11 May 1977)

A model potential for gas–solid interactions has been used to investigate the dynamics of recombination of two atoms initially adsorbed on a solid surface. In the spirit of Polanyi's investigation into the effect of the potential energy surface on the dynamics of gas-phase reactions, a range of gas–solid potential energy surfaces has been constructed. Classical trajectories have been used to study the dynamics of reactions on those surfaces. It has been found that many of the rules postulated by Polanyi for energy requirements and disposal mechanisms for gas-phase systems are applicable also to the case of recombination of adsorbed atoms to form a gas-phase molecule. Previous work assumed a rigid surface providing a static background potential in which the adsorbed atoms moved. An extension of this model is described in which the rigid surface restriction is relaxed and one or more surface atoms are allowed to move interacting with the adsorbed atoms. Using this potential the rigid surface model is shown to be a good approximation for describing many aspects of recombination dynamics.

I. INTRODUCTION

A large part of gas-phase chemical dynamics is concerned with specific energy requirements and specific energy disposal mechanisms in chemical reactions. It is now abundantly clear that not all types of energy are equally efficient in promoting endothermic reactions, nor are all channels of energy disposal equally efficient in exothermic reactions.[1] To assist in understanding the microscopic details of such energy specificity, Polanyi and co-workers initiated a series of model calculations.[2] Much of their work used several simplifying assumptions: (a) classical trajectories were used; (b) atom–diatom exchange reactions were studied; and (c) purely empirical potentials were used allowing them to model a wide range of realistic (if not actually existing in nature) potential energy surfaces. The resulting "propensity rules" have found wide applicability in chemical dynamics. Most of the essential features of these propensity rules have survived the test of more refined calculations. The great utility of these rules lies precisely in their qualitative nature and broad applicability (e.g., attractive potential surfaces lead to vibrational excitation of the products). Therefore, it is not surprising that relatively simple calculations proved sufficient to obtain the broadest principles of energy specificity.

We have recently developed a model potential to describe the interaction of diatomic[3] and triatomic[4] molecules with rigid (frozen-lattice) solid surfaces. Using these potentials, classical trajectories have been calculated to study selected features of the dynamics of atomic recombination,[5] atom–adsorbed atom collisions,[6] molecule–surface collisions,[7] and molecule–adsorbed atom collisions.[4] The thrust of this work has been to elucidate what novel dynamical effects (i.e., energy specificity) may be present in chemical reactions occurring on solid surfaces and to what extent the propensity rules developed for gas-phase reactions are also applicable to surface reactions. It is well known (and of considerable economic importance) that solid surfaces often drastically affect the kinetics of chemical reactions. Although reaction rates are considerably affected, relatively little attention has been paid to how dynamics (i.e., specific energy requirements) are changed by the use of heterogeneous catalysts. Computer simulations, in the spirit of Polanyi's work in gas-phase dynamics, are well suited to exploring this question.

For the interaction of a diatomic molecule with a solid, a first approximation could be to use gas-phase information for A+(B, C) collisions, but permit one atom to become infinitely massive, thus mimicking a solid. With this assumption, one would expect heterogeneous reaction dynamics to be simply a subset of gas-phase dynamics. However, there are two complicating factors: (1) When energy transfer to or from the solid is present, the dynamics could be affected in ways not predicted by simple A+(B, C) dynamics. (This degree of freedom was not present in our previous work employing the rigid surface model. However, surface dynamics is included in certain of the calculations described below.) (2) A more fundamental difference, present also in the rigid surface approximation, is that the size (as well as the mass) of one collision partner becomes infinite. Therefore, it is possible (and occurs frequently in our calculations) that two atoms can both be close to the solid, but arbitrarily far from each other. This introduces an additional asymptotic scattering channel which has no good analogue in gas-phase collisions of simple molecules. (The extent to which unimolecular decomposition or collision complexes of large molecules mimic gas-solid reaction dynamics is not clear. Certainly, gas–solid collisions and atom–diatom collisions are two limiting cases for which interesting dynamical effects could be studied. There are numerous intermediate cases.) As discussed below, in spite of these complications, many of the Polanyi rules for simple gas-phase reactions can be formulated in a way appropriate for the class of surface reactions studied below.

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In the present study, we investigate the dynamics of recombination of two atoms initially adsorbed on a solid surface. In the spirit of Polanyi's investigation into the effect of the potential energy surface on the reaction dynamics for gas-phase systems,[2] we use a range of gas–solid potential energy surfaces generalizing our previous studies of recombination dynamics.[5] Also, we present preliminary results for heterogeneous reaction dynamics in which the surface atoms themselves are permitted to move. For the cases studied, no significant changes result from motion of the surface atoms. Section II gives a brief overview of the propensity rules developed for gas-phase collisions. Section III reviews the model potential for gas–surface collisions and describes the range of potentials used here. Section IV presents results and discussion for the rigid surface model. The generalization to a moving surface is given in Sec. V, and preliminary results are presented.

II. OVERVIEW OF GAS-PHASE PROPENSITY RULES

For exothermic reactions $A+BC-AB+C$ with exothermicity in the range 30–50 kcal mole^{-1} and activation barriers typically around a few kcal mole^{-1}, it was shown that attractive potential surfaces, where the energy is released as A approaches B, lead to vibrational excitation of the product molecules; repulsive surfaces, where the energy is released as AB separates from C, give rise to rotation and translation of the products. An exception to this was found to occur for repulsive surfaces when the attacking atom A was very much heavier than atom C. This leads to "mixed energy release" dynamics and product vibrational and rotational excitation. Complex collisions, where more than one encounter between reagents or products takes place, were also found to deviate from the rule. Such secondary encounters mainly occur on attractive surfaces and tend to reduce the product vibrational excitation on highly attractive surfaces.

Polanyi and co-workers also examined the effect of the position of the crest of a barrier for thermoneutral reactions. It was found that "a barrier along the approach coordinate is most efficiently surmounted by motion along the approach coordinate (reagent translation) whereas a barrier along the coordinate of separation is most efficiently surmounted by motion along that coordinate (reagent vibration)."[2] The converse was found to be true for energy hollows rather than barriers. These effects were found to be independent of the masses of the particles.

For endothermic reactions where the crest of the barrier is located in the exit valley, it was found that vibrational energy in the bond under attack was necessary for successful reaction. An exception to this was when C had a much smaller mass than A or B, in which case too much vibration in the reagents markedly reduced the probability of reaction.

These results were concluded from series of classical trajectory calculations on London–Eyring–Polanyi–Sato[6] (LEPS)-type potential functions for gas-phase triatomic systems. The aim of the present work is to investigate in a similar manner the effect of the form of the potential energy function on the dynamics of reactions on solid surfaces. Reactions on solid surfaces can be thought of in three steps: (1) adsorption of the gas on the solid; (2) possible equilibrium, or partial equilibration of the adsorbed particles with the solid; (3) recombination and desorption of a gas molecule. If the adsorption and recombination steps are fast compared to the adsorbate–lattice relaxation time, Step 2 can be neglected. The circumstances under which this occurs are the circumstances under which the rigid surface model should be applicable. This is discussed more fully in Sec. V.

The purpose of the present study is to attempt to model the internal vibration–rotation states of diatomic molecules as they are formed and desorb from the surface and to understand which features in the potential lead to what internal states. As Polanyi first discussed for gas-phase exothermic reactions,[9] circumstances exist in which useful amounts of the reaction energy appear as vibration in the products. A further goal of the present computer simulations is to explore (admittedly, in a very crude way) possible situations under which similarly useful vibrational populations might be obtained from heterogeneously catalyzed reactions. The function of a catalyst is to change the energetics of the reaction path to accelerate the formation of products. Similarly, a change in the energetics of the reaction path will affect the distribution of the available energy in the products. It is this modified energy distribution we will attempt to model.

We envision attempting to simulate the following process: consider a (hypothetical) reaction of gas molecules that is highly exothermic but, for whatever reason, does not produce the desired state distribution of products. A catalyst is used that alters the energetics of the reaction path and produces some other product state distribution. The available energy comes from the gas-phase reagents with the solid remaining chemically and dynamically inert throughout the reaction. (We will relax the restriction that the solid be strictly rigid in Sec. V, but we will assume that virtually all the available energy comes from the gas-phase reagents. The extent that the solid is an energy sink under these conditions will be discussed in Sec. V.) While the temperature of the solid can often affect its catalytic activity, it is usually assumed that the primary mechanism is that of a hot surface effectively lowering activation barriers more than a cold surface. Since this does not require gas–surface energy transfer, it too can be treated with either the rigid surface or the moving surface model.

Hence, we are concerned with basically a two-step process: adsorption followed by recombination and desorption with a net energy release into the products and possibly into the solid. The present work considers only the recombination processes to assess how the potential surface affects the product state distributions. The dynamics of the adsorption process determine the initial conditions for the recombination (i.e., the initial momenta of the adsorbed atoms when they collide) and therefore is one step further removed from the formation of products. The effect of various initial momenta on product state distributions is the subject of a future study.

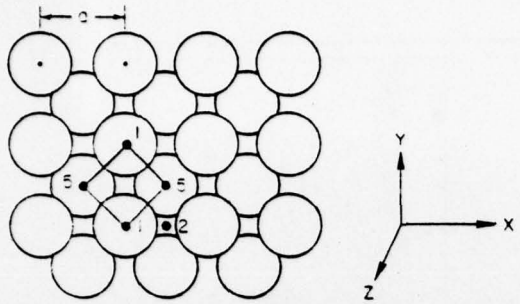


FIG. 1. Geometry of the W(001) surface indicating the singly coordinated (1*CN*) adsorption site and the 2*CN*, 5*CN* sites. The origin of coordinates is at a 1*CN* site with the x–y plane parallel to the surface and the x axis directed towards a neighboring 1*CN* site. To study recombination dynamics, two atoms are given random initial momenta, subject to the restriction that the (x, y) components of momenta lie within the square indicated. This neglects "catch-up" collisions. $a = 5.97$ a.u.

We have also considered the question: how many, if any, of the "Polanyi rules" for gas-phase dynamics are applicable also to gas–surface dynamics, in particular to recombination dynamics? For example, in an exothermic recombination reaction is it true that an attractive potential surface will give rise to vibrational excitation of the product molecule? The potential functions used throughout this work have the form of the modified LEPS potential that has been used in previous studies of gas–solid interactions.[3–7] By varying the parameters in the potential function we generate a wide variety of potential surfaces. We use both equal mass and unequal mass combinations. We have relaxed the rigid surface approximation in part allowing some of the surface atoms to move, and we examine the effect of the surface motion on the recombination dynamics.

III. INTERACTION POTENTIALS: RIGID SURFACE

The potential functions used were generated from the diatom–solid surface modified LEPS potential that has been used in previous work.[3–7] This has the form

$$V_{\mathrm{LEPS}} = U_1 + U_2 + U_3 - [A_1^2 + (A_2 + A_3)^2 - A_1(A_2 + A_3)]^{1/2}, \tag{1}$$

where

$$U_i = \frac{D_i}{4(1+\Delta_i)} \{(3+\Delta_i)\exp[-2\alpha_i(r_i - r_{i0})] - (2+6\Delta_i)\exp[-\alpha_i(r_i - r_{i0})]\}, \tag{2}$$

$$A_i = \frac{D_i}{4(1+\Delta_i)} \{(1+3\Delta_i)\exp[-2\alpha_i(r_i - r_{i0})] - (6+2\Delta_i)\exp[-\alpha_i(r_i - r_{i0})]\}, \tag{3}$$

and D_i, α_i, and r_{i0} are the dissociation energy, Morse parameter, and equilibrium distance for the ith two-body interaction. We take $i = 1$ to be the atom–atom interaction and assume a typical H_2 Morse curve to obtain the parameters D_1, α_1 and r_{10}. Δ_1 is used as a parameter to generate different potential surfaces. $i = 2$, 3 correspond to the atom–surface interactions, and it is assumed that these are the same for both atoms. To account for the structure of the solid in the atom–surface interactions we require the parameters D, α and r_0 to be functions of x and y, where the x–y plane is parallel to the plane of the solid surface. The symmetry assumed for the surface is that of the (100) face of a bcc solid and the geometry is that of tungsten (see Fig. 1). Following the previous work of H_2 interacting with the (100) face of tungsten, we assume the existence of three possible binding sites, the on-top (1*CN*), bridge (2*CN*), and hole (5*CN*) sites. We take

$$D(x, y) = D_0[1 + \delta Q(x, y)], \tag{4}$$

$$r_0(x, y) = Z_m[1 + \epsilon P(x, y)], \tag{5}$$

where

$$Q(x, y) = k\left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right)\right] - A\left[\cos\left(\frac{2\pi x}{a}\right) - 1\right]\left[\cos\left(\frac{2\pi y}{a}\right) - 1\right], \tag{6}$$

$$P(x, y) = k\left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right)\right] - B\left[\cos\left(\frac{2\pi x}{a}\right) - 1\right]\left[\cos\left(\frac{2\pi y}{a}\right) - 1\right]. \tag{7}$$

a is the tungsten nearest neighbor distance (= 5.97 a.u.). k is chosen to be either 0 or 1; in the previous work it was always assumed to be 1. The effect of $k = 0$ is to introduce channels into the egg-carton shape of the surface by making the on-top and bridge sites identical for hydrogen binding. The Morse parameter α is chosen as before to be $[0.02894/D(x, y)]^{1/2}$, where D is in atomic units of energy giving α in atomic units of inverse length

We have a total of nine parameters with which to generate different potential surfaces, namely, D_0, δ, k, A, Z_m, ϵ, B, Δ_1, $\Delta(=\Delta_2=\Delta_3)$. The parameters were adjusted to give nine different potential energy surfaces with varying barriers and modes of energy release. These parameters are given in Table I. Equipotential

TABLE I. Parameters used in generating the various potentials.

Potential	ϵ	Z_m	δ	D_0	k	A	B	Δ_1	$\Delta_2 = \Delta_3$	Binding energy (eV) 1*CN*	2*CN*	5*CN*
I	1.0	3.12	1.0	0.1102	0.0	0.1067	0.2051	0.147	0.03	3.0	3.0	1.72
II	0.2112	2.19	0.0474	0.1007	1.0	1.463	0.653	0.147	0.03	3.0	2.74	1.72
III	0.2112	2.19	0.0474	0.1007	1.0	0.1463	0.653	−0.1	−0.1	3.0	2.74	2.40
IV	1.0	3.12	1.0	0.0551	0.0	0.1067	0.2051	0.147	0.03	1.5	1.5	0.86
V	1.0	3.12	1.0	0.0551	0.0	0.1067	0.2051	0.3	0.3	1.5	1.5	0.86
VI	0.2112	2.19	0.0474	0.0503	1.0	1.463	0.653	0.147	0.03	1.5	1.37	0.86
VII	1.0	3.12	1.0	0.0551	0.0	0.1067	0.2051	0.0	−0.3	1.5	1.5	0.86
VIII	1.0	3.12	1.0	0.0551	0.0	0.1067	0.2051	0.147	0.3	1.5	1.5	0.86
IX	0.2112	2.19	−0.1961	0.0503	1.0	−0.3725	0.653	0.147	0.03	0.86	1.37	1.5

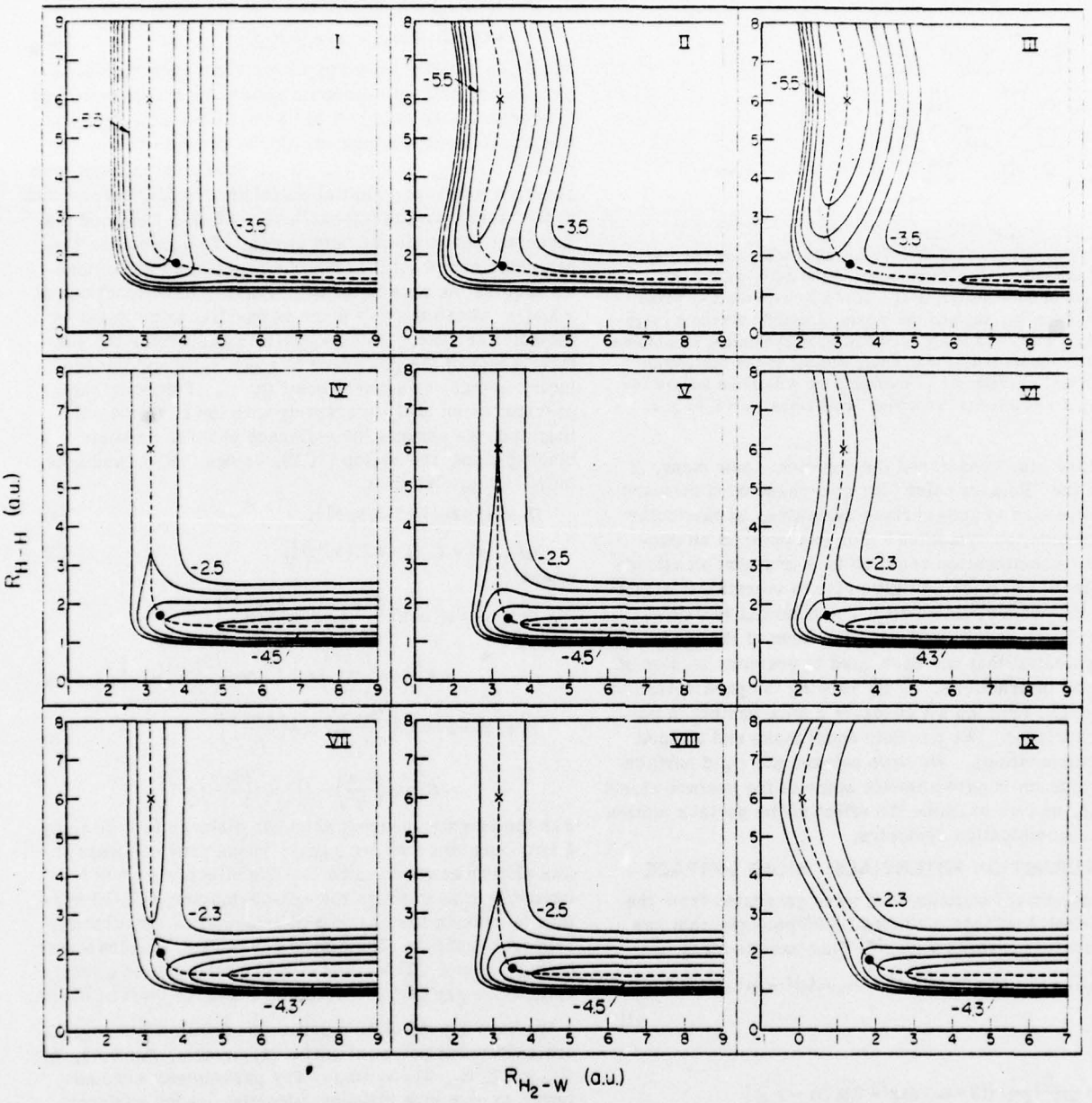


FIG. 2. Equipotential contours (in eV) for the approach of H_2 to W(001) for the different potential surfaces studied. The contour levels are equally spaced for any given potential surface. The H–H bond is parallel to the plane of the surface. The center of mass of the molecule is perpendicularly above a 2*CN* site. *X* indicates the position of the reactants, two atoms adsorbed at adjacent 1*CN* sites (5*CN* for IX). • locates our choice of the "transition site."

contour plots are given in Fig. 2. These are for a hydrogen molecule approaching the surface with the axis parallel to the plane of the surface. The midpoint of the bond is perpendicularly approaching a bridge (or 2*CN*) site and the bond is stretching symmetrically in the direction of the atomic adsorption site of greatest stability. This is the on-top (1*CN*) site for all the potential surfaces except IX, where the hole site (5*CN*) is the most stable site. With the coordinate system of Fig. 1, the bond in potential IX is stretching parallel to the *x* axis along the line $y = a/2$, while for the other potential surfaces, it is stretching along the *y* axis. The dashed line indicates the minimum energy reaction path from the reactants, two atoms adsorbed on the surface, to products, a molecule far from the surface. The *X* marks the initial position of the atoms in the 1*CN* or 5*CN* sites. The energy along the reaction path is shown in Fig. 3. The dashed line parallel to the ordinate indicates the position along the reaction path of an arbitrarily defined "transition state" between reactants and products. While this transition state is not well defined for these molecule–surface potential functions, it is a con-

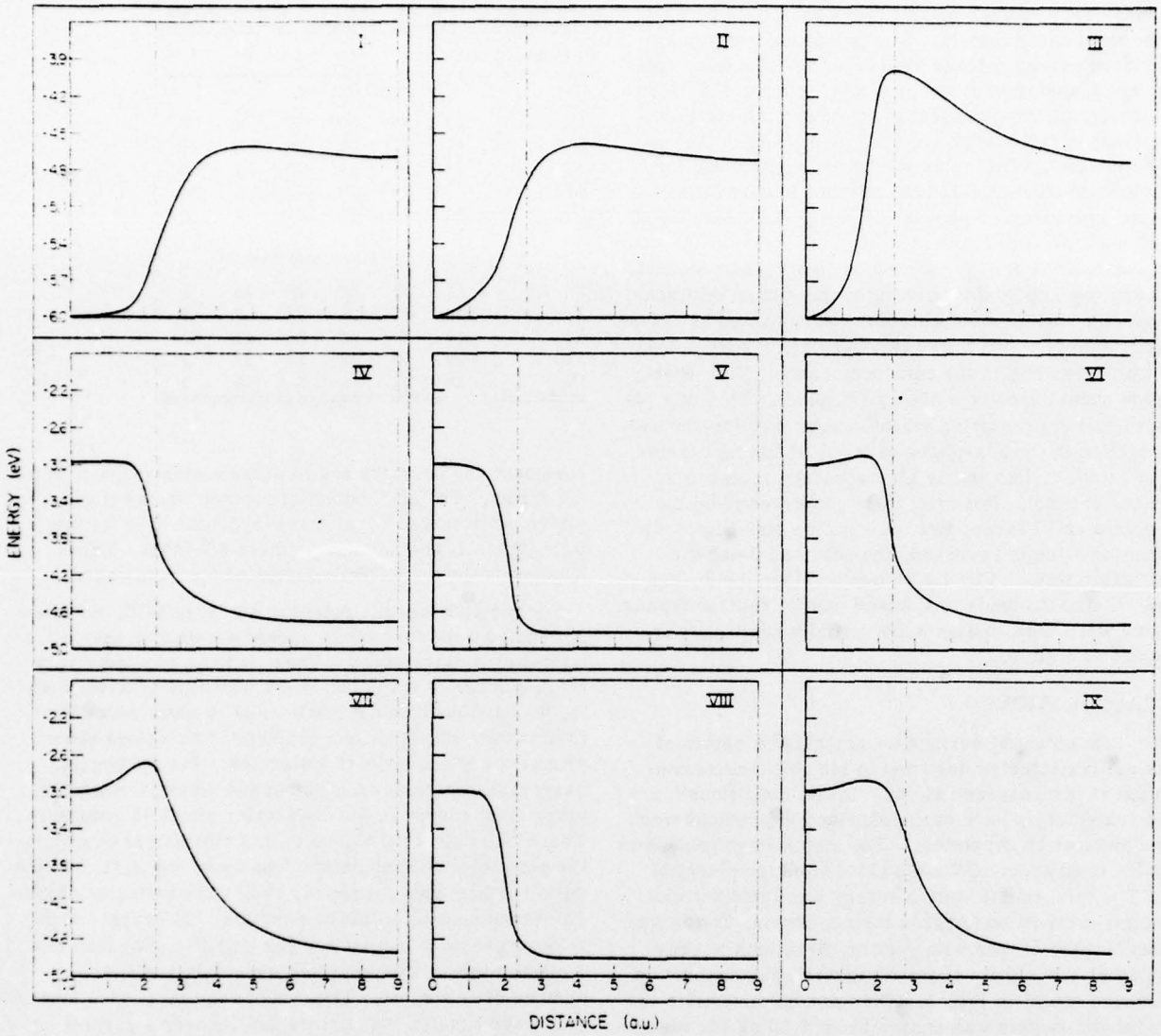


FIG. 3. Energy profiles along the reaction paths for the potential surfaces given in Fig. 2. The dashed line marks the region of transition from reagents to products (denoted by ● in Fig. 2).

cept useful for defining the boundary between entrance and exit channels and therefore plays a role in any discussion of the effects of barrier position in relation to these channels. Consequently, we have chosen to determine the transition state region approximately for each potential surface. In potentials IV, V, and VIII the distance along the reaction path of the transition state region is easily defined since the reaction path makes quite a sharp turn at that point. For the other potentials, the exact position is not clearly defined but we chose it to be approximately half-way around the curve in the reaction path in the transition state region.

Potentials I–III are endothermic with endothermicity of approximately 1.26 eV. We assume that the overall reaction catalyzed by the solid surface is exothermic. However, it may occur that the adsorption step releases more energy than the total reaction. Therefore, the recombination will occur between atoms with considerable translational energy, but on an uphill reaction path. Potentials I–III are intended to model this possibility. Potential I has the crest of the barrier (of height 1.39 eV) in the exit channel. The on-top and bridge sites are identical for this case and are more stable than the hole site. II also has the crest of the barrier (of height 1.39 eV) in the exit channel. The adsorption sites, in order of decreasing stability, are on-top, bridge, and hole. For gas-phase reactions on potential surfaces of this form, vibrational energy in the bond under attack is necessary for successful reaction. It is not immediately obvious what analogous condition on the gas–solid potentials will be necessary for successful recombination. Potential III is also endothermic but has the crest of the barrier (of height 1.99 eV) at more or less the transition state position.

The remaining potential functions are exothermic with exothermicity of approximately 1.73 eV. Potential IV

has no barrier to molecule formation and desorption, and the energy release occurs about equally in both enterance and exit channels. For gas-phase reactions, this mixed energy release would lead to vibration, rotation, and translation of the products. Potential IV also has no barrier from reagents to products but for this case much of the energy release takes place in the entrance channel. This is an attractive surface and for gas-phase systems would lead to vibrationally excited product molecules. Potential VI has a small barrier of height 0.10 eV entirely in the entrance channel. As with IV about half the energy release occurs in each channel. If an analogy can be drawn with the gas-phase reactions, the barrier will be most efficiently surmounted by translational energy . VII also has a barrier (of height 0.33 eV) with crest just in the entrance channel. The energy release occurs mostly in the exit channel. This is a repulsive surface requiring vibrational energy for successful reaction in the gas-phase case. VIII has no barrier and, as with V, has nearly all the energy released in the entrance channel. Potential IX is generated from the same data as VI except that the relative stability of the adsorption sites is reversed, the hole site being the most stable followed by the bridge and then the on-top sites. This also leads to a mixed energy release type of surface when the two atoms are initially positioned at adjacent hole sites.

IV. CALCULATIONS

For each potential surface we computed a series of classical trajectories designed to simulate the recombination of two adsorbed atoms. Initial conditions for those trajectories have been described in previous work on recombination dynamics.[5] The atoms were positioned initially at adjacent $1CN$ sites ($5CN$ sites for potential IX). The total initial kinetic energy was fixed but was randomly distributed between the two atoms. The initial momenta were chosen with random directions but restricted so the x and y components were directed within the square shown in Fig. 1. The total initial kinetic energy for the system was chosen to be 3.50 eV for the endothermic potential surface and 0.50 eV for the exothermic surfaces. These values are sufficiently large to surmount any barriers and to allow a wide range of product states. For each potential surface we ran trajectories for atoms of equal mass (hydrogen) and for one light (mass 1) and one heavy (mass 80) atom. Three hundred trajectories were computed for each case.

TABLE II. Mean distribution of energy in product molecules.

Potential	% Molecule formation	% E_{vib}	% E_{rot}	% E_{trans}
	(a) Equal masses			
IV	33	43	15	42
V	35	57	23	20
VI	33	50	10	40
VIII	29	61	20	19
IX	32	49	5	46
	(b) Light–heavy mass combination			
IV	24	46	12	42
V	39	44	34	22
VI	37	52	13	35
VIII	26	45	32	23
IX	40	30	20	50

TABLE III. Product vibrational state distribution (%) summed over rotational sublevels.

Potential	$v=0$	1	2	3	4	5
	(a) Equal masses					
IV	18	39	30	12	1	0
V	11	17	36	34	3	0
VI	8	36	39	15	2	0
VIII	1	20	48	26	5	0
IX	14	29	32	24	1	0
	(b) Light–heavy mass combination					
IV	11	20	20	30	15	4
V	15	21	26	22	7	9
VI	10	10	23	23	25	10
VIII	18	23	13	13	27	8
IX	39	22	14	20	3	2

For the endothermic potential surfaces I–III, very few molecules were formed for either the equal mass or the light–heavy mass cases. Thus, without running a very large number of trajectories (as was done in Refs. 6 and 7), we have insufficient numbers of product molecules to draw any statistically meaningful conclusions about properties of the product molecules. For successful gas-phase reactions on endothermic potential surfaces, vibrational energy in the bond under attack is necessary. There is no direct analogue of this vibrational energy in the gas–solid recombination dynamics, but motion on the solid surface does not appear to be sufficient for successful recombination on such potentials. Of course, even a low probability of reaction per collision may lead to molecule formation and desorption after a sufficient number of collisions. This would require a much longer residence time on the surface and, hence, a greater possibility for gas–solid energy transfer. Such equilibration with the surface is inconsistent with the constraints of our model and, therefore, actually running large numbers of trajectories is not likely to contribute to an understanding of the processes. We conclude that endothermic desorption processes appear to be relatively inefficient at forming molecules, even with considerable kinetic energy. Increased energy transfer with the solid is expected and hence increased "leakage" of reaction energy on the way from reactants to products is also expected. Therefore, reactions with very strongly bound intermediates are not likely candidates to channel energy efficiently into the product molecules.

Tables II and III give the results of the trajectory calculations on the exothermic surfaces. Potential VII is not included since in this case also an insufficient number of molecules were formed. This is a repulsive surface, having most of the energy released in the exit channel, and in the gas phase such a surface also requires vibrational energy in the bond under attack for successful reaction. While there seems to be no gas-

solid analogue to such vibrational energy, we have again found that translation over the surface (including components of motion perpendicular to the surface) is not sufficient despite the exothermicity of the reaction. For the remaining exothermic potential surfaces approximately one-third of the trajectories led to reaction and the formation of a product molecule. The total energy available to these molecules for internal excitation (including zero-point energy) and translation is about 2.25 eV. Table II gives the mean distribution of this energy between vibration, rotation, and translation. Table III gives the vibrational state distributions summed over the rotational sublevels of the desorbed product molecules. For the case of two hydrogen atoms, the attractive potential surfaces V and VIII lead to considerable vibrational excitation, as is the case for attractive surfaces in gas-phase reactions. These surfaces also lead to the most rotational excitation of the products (and hence the least translational energy, consistent with the attractive potential surfaces). Potential IV is a mixed energy release surface and leads to just about equal amounts of energy in vibration and translation. This can be regarded as analogous to the gas-phase results for mixed energy release surfaces. Potentials VI and IX are also mixed energy release but each has a small barrier in the entrance channel. The initial translational energy of the adsorbed atoms is seen to be adequate to surmount these barriers, again consistent with gas-phase results. VI and IX differ only in the relative ordering of the adsorption sites and this difference seems to have little effect on the recombination properties of the surfaces.

The light–heavy mass combination has the effect of smoothing out the sharper peaks in the vibrational state distribution. For the mixed energy release potentials IV and VI (which for H_2 peak around $v=1$, $v=2$) this causes the mean vibrational energy to increase very slightly. For the other potentials which peak around $v=2$, $v=3$, the mean vibrational energy is decreased considerably by this smoothing. The proportion of energy that occurs as translation of the product molecules varies little with the mass combination. For the light–heavy case this means a much smaller velocity of the molecule, and indeed these trajectories took much longer to compute than did the equal (light) mass case. Since the translational energy is roughly the same for the two mass cases, the change in mean vibrational energy is reflected in a change in mean rotational energy. The unequal mass case gives rise to increased rotational energy for the attractive potentials surfaces V and VIII and also for the mixed energy release surface IX. Potentials VI and IX differ only in the relative ordering of the adsorption sites and give similar results for equal masses, but for light–heavy mass combinations IX gives rise to significantly less vibrational excitation than VI and correspondingly more rotation and translation.

V. MOVING SURFACE

The rigid surface model was previously justified[3] by the assumption that the adsorbed atoms encounter each other and recombine (or not) on a time scale short compared to adsorbate–lattice energy transfer times. For light adsorbates and heavy surface atoms, it was felt that the mass difference would ensure only modest energy transfer. Our previous estimates were 2% energy transfer for H atom–tungsten interactions,[5b] or about 4% for H_2–tungsten interactions. However, since we are using heavier adsorbate atoms in some of the present calculations, it is appropriate to investigate more carefully the validity of the rigid surface model. Therefore, we have run trajectories with the rigid surface restriction relaxed and some of the surface atoms allowed to move.

It is first necessary to generalize V_{LEPS} (the LEPS potential for the interaction of a gas molecule with a rigid solid surface). In addition to a gas–rigid surface interaction, V_{LEPS} can also be considered as the interaction of a gas molecule with the lattice sites of the solid. If we allow motion of the solid atoms, at any instant those atoms may or may not be at a lattice site. Therefore, we have modified V_{LEPS} by introducing correction terms:

(1) V_R, the restoring force on each atom of the solid, tending to return it to its lattice site;

(2) V_{CORR}, to account for the change in the gas–surface interaction when the solid atom is displaced from its lattice site.

We have

$$V_{total} = V_{LEPS} + V_R + V_{CORR} . \tag{8}$$

V_R and V_{CORR} must vanish when all the solid atoms occupy their lattice positions. We have used pair potentials for V_R and V_{CORR} to correct V_{LEPS} in an approximate way to allow for motion of the solid atoms. Assuming that V_R binds the solid atom to its lattice site constitutes an Einstein model of the solid. Certainly, pairwise atom–atom interactions can be used for V_R, and are commonly used to simulate properties of bulk solids.[10] However, we feel that the simplicity of the Einstein model, and the corresponding savings of computer time, is justified for the present rough estimates of energy transfer. More refined energy transfer calculations, using a generalized Langevin oscillator model for the solid, demonstrate that the Einstein model is a reasonable first approximation for short collision times.[11]

The model does not include the nonadditive corrections for the solid–solid interactions, or the nonadditive corrections to V_{CORR}. For the restoring force V_R we have used a harmonic potential binding an atom of the solid to its (fixed) lattice site. To account for the change in the gas–solid potential due to displacement of the surface atom from its lattice site, we have used a pair potential for V_{CORR} connecting each gas atom with each surface atom. V_{LEPS} already contains the interaction of each gas atom with each lattice site, so to avoid including it twice, this lattice site interaction must be subtracted from V_{CORR}. We take

$$V_{CORR} = \sum_{g}^{N_g} \sum_{s}^{N_s} [\, W(R_{g-s}) - W(R_{g-l}) \,], \tag{9}$$

where N_g is the number of gas atoms, N_s is the number

TABLE IV. Mean distribution of energy in product molecules: (a) rigid surface; (b) two surface atoms free to move.

Potential		% Molecule formation	$\% E_{vib}$	$\% E_{rot}$	$\% E_{trans}$	% Energy transfer
		(a) Equal masses				
IV	(a)	41	41	15	44	
	(b)	72	49	11	34	6.32
V	(a)	36	60	20	20	
	(b)	78	52	26	15	6.69
VI	(a)	42	51	10	39	
	(b)	65	57	8	30	5.24
VIII	(a)	30	68	18	14	
	(b)	69	62	18	13	7.04
		(b) Light–heavy mass combination				
IV	(a)	21	47	13	40	
	(b)	73	51	10	34	4.79
V	(a)	40	49	30	21	
	(b)	79	37	40	19	3.86
VI	(a)	40	51	13	36	
	(b)	69	47	17	32	5.89
VIII	(a)	26	37	40	23	
	(b)	70	46	27	23	4.26

of solid atoms that are free to move, R_{g-s} is the distance between the gas atom and the solid atom, and R_{g-l} is the distance between the gas atom and the lattice site of the solid atom. As required, if the surface atom occupies its lattice site, $R_{g-s} = R_{g-l}$ and $V_{CORR} = 0$. The total gas–solid potential for the moving surface case is

$$V_{total} = V_{LEPS} + \sum_{s}^{N_s} V_R^s + \sum_{g}^{N_g} \sum_{s}^{N_s} [W(R_{g-s}) - W(R_{g-l})], \qquad (10)$$

where V_R^s is the harmonic restoring force for solid atoms.

To summarize, the revised model includes

(1) all forces, pairwise and nonpairwise, to describe the interaction of a gas molecule with a surface when the surface atoms are fixed at their lattice sites;

(2) pairwise corrections for the motion of the solid atoms away from their lattice sites;

(3) pairwise corrections to account for the change in the gas–solid potential due to displacement of the surface atoms from their lattice sites.

We have used this potential to examine the validity of the rigid surface approximation for the recombination studies. We require the harmonic restoring force for the solid atoms, and the gas–solid atom Morse potential [W in Eq. (9)]. For the harmonic restoring force we need an estimate of the Einstein temperature of the surface. The Einstein temperature can be estimated from the Debye temperature either by requiring the best single-oscillator approximation to the Debye mode density[11] or by expanding the high temperature Debye and Einstein heat capacities and matching terms through T^{-2}. In both cases, one finds the Debye temperature to be smaller than the Einstein temperature by a factor of $\sqrt{0.6}$. Also, in order to correct approximately for the smaller Debye temperature of the surface compared to the bulk, an extra factor of (2/3) is used.[12] Hence,

$$\theta_{Einstein}^{(surface)} = (2/3)\sqrt{0.6}\ \theta_{Debye}^{(bulk)} \qquad (11)$$

Using $\theta_{Debye}^{(bulk)} = 400\,^{\circ}K$ yields $\theta_{Einstein}^{(surface)} = 210\,^{\circ}K$. This gives a harmonic force constant for a tungsten solid atom of 0.074 a.u. The solid atoms were assumed initially to be at their equilibrium positions and those that were free to move were given an initial kinetic energy (the same for all the atoms) equal to the average energy of the harmonic oscillator at a surface temperature of 300 °K with an Einstein temperature of 210 °K. Then each solid atom initially has kinetic energy of 0.00197 a.u.; the initial direction of velocity of the atoms was randomly chosen so that there was equal probability of it being within any differential solid angle. The gas–solid Morse potential used in V_{CORR}, $W(R_{g-s})$, was chosen to have $\alpha = 0.5123$ a.u.; $D = 0.055$ a.u. and $r_0 = 3.12$ a.u. These parameters correspond to the hydrogen atom–tungsten 1*CN* Morse potential for the surfaces used.

To examine the validity of the rigid surface model in recombination dynamics, 100 trajectories were computed for each of potentials IV, V, VI, and VIII and for both the equal (light) mass and the light–heavy mass combination. The initial conditions of the adsorbed gas atoms were chosen to be the same in these trajectories as in the first 100 trajectories for those potentials in the rigid surface model. Two surface atoms were allowed to move, those being the two atoms in the 1*CN* sites directly below the adsorbed gas atoms in their initial configuration. The initial directions of velocity of these two surface atoms were randomly selected. Table IV shows a comparison of the results of these trajectories for the rigid surface and for the moving surface cases. It is not clear why the moving surface atoms seem to increase the total probability of molecule formation by a factor of 2. The energy transferred between the gas atoms and the surface atoms for both the equal and unequal mass cases was, in the mean, 4%–7% of the total energy available to the product molecules. The mean distribution of the available energy among vibration, rotation and translation is changed very little by the motion of the surface. More work is needed to assess carefully the role of surface motion on angular distributions (which measures momentum transfer and are frequently a more sensitive probe of collision dynamics) as well as the interaction of surface atoms and adsorbate atoms with comparable masses. The generalized Langevin oscillator model of Adelman and Doll[13] could be included to mimic the effects of the full lattice on the reaction zone. The present studies indicate that the product state distributions of recombining atoms are not very sensitive to the motion of the surface atoms.

VI. CONCLUSION

From the above calculations we conclude that many of the rules postulated by Polanyi for gas-phase energy requirements and disposal mechanisms are applicable also to recombination of adsorbed atoms for gas–solid interactions. We have found that repulsive potential surfaces which in the gas-phase require vibrational energy in the bond under attack for reaction do not lead to reaction for

heterogeneous recombination. This is true also for endothermic potential surfaces. Attractive potential surfaces give rise to more vibrational excitation in the product molecules and less translational energy than do mixed energy release surfaces. However, the light–heavy mass combination was found to remove the increase in vibrational excitation found in attractive rather than mixed energy release surfaces. The energy is channeled instead into rotational excitation. The mixed energy release surfaces give rise to more translational energy, consistent with Polanyi's result. The rigid surface was found to be a good approximation for calculating product state distributions in these recombination studies.

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APPENDIX B

"VIBRATIONAL EXCITATION FROM HETEROGENEOUS CATALYSIS"

VIBRATIONAL EXCITATION FROM HETEROGENEOUS CATALYSIS*

by

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Abstract

Classical trajectories have been used by numerous researchers to investigate the dynamics of exothermic chemical reactions (atom + diatom) with a view towards understanding what leads to vibrational excitation of the product molecule. Unlike these studies, we consider the case where the reaction is catalyzed by a solid surface. The trajectory studies indicate that there should be conditions under which considerable vibrational energy appears in the product molecules without being lost to the solid during the course of the reaction.

I. Introduction

There have been experimental indications that for atomic recombination on solid surfaces, energy is disposed of in highly specific ways.[1,2] For example, in recombination of oxygen on a variety of metal surfaces, the data indicated that most of the reaction energy was often deposited into the gas phase diatomic molecule.[2] This was in contrast to conventional ideas that there was essentially equilibrium partitioning of energy between gas and solid for atomic recombination. Recent data by Halpern and Rosner[1] clearly confirm the specific nature of energy disposal in heterogeneous reactions for recombination of atomic nitrogen on a variety of metals. The data is sufficiently precise and reproducible that some hypothesis about the chemical dynamics of recombination reactions on surfaces could be proposed. It had been known for some time that when molecules react in the gas phase, various modes of energy disposal (i.e., as vibration, rotation, or translation in the products) are not all equivalent.[3] Whether or not a large fraction of the reaction energy appears as product translation or vibration is known to be determined by the detailed energy contour along the reaction path, relative masses of the atoms, and other subtle features of the potential.[4] A reaction occurring on a solid surface shares many of the same features. A reaction path can be constructed, the energetics along this path can be described and the dynamics of the resulting reaction can, in principal, be studied. The sole complicating feature is the presence of a solid surface upon which the reaction occurs. Therefore, it is not surprising that heterogeneous reactions would exhibit preferred modes of energy disposal. Precisely how the solid surface complicates

the dynamics of heterogeneous reactions is far from clear, but the fact that interesting dynamical effects exist in heterogeneous reactions seems beyond dispute.

One of the most useful consequences of specific energy disposal in gas phase reactions has been the formation of vibrationally excited product molecules and resulting infra-red chemical lasers.[5] The question naturally arises whether reactions promoted by a heterogeneous catalyst can lead to equally useful vibrational population inversions. Various experimental groups[1,2] have been led to speculate that a large fraction of the available reaction energy does appear as product vibration, but the experimental support is extremely fragile.

In analogy with similar studies for gas-phase dynamics, we have undertaken a series of computational studies attempting to model vibrational excitation in heterogeneous reactions. Our method for approaching this problem has followed closely the theoretical methods (i.e., classical trajectories on a series of model potentials) whereby the behavior of gas phase chemical lasers was elucidated. Since these methods were productive for gas phase chemical lasers, there is reason to believe they will also lead to important insights into heterogeneous chemical dynamics and vibrational excitation. Because of this close analogy, we think it is productive to review briefly the history of gas phase chemical lasers to point out the reasons for our current studies, and by learning from history, we hope to indicate likely future directions for heterogeneous chemical dynamics.

Polanyi and co-workers observed vibrational population inversion via infra-red chemiluminescence in HCl formed from the reaction of H + Cl_2. The possibility of constructing an infra-red laser was explicitly discussed

in a paper submitted for publication in 1960.[6] An extensive series of classical trajectory studies on a model potential surface (LEPS) was undertaken in order to understand the conditions under which vibrational population inversion could be expected in exothermic reactions. The first results were submitted for publication in 1962,[7] and a detailed discussion of energy release in exothermic reactions appeared in 1966.[4] Various features in the potential energy surface in addition to exothermicity were shown to be necessary for efficient population inversions to occur. Acting on Polanyi's 1960 prediction, Kasper and Pimentel[8] produced the first chemical laser in 1965 using the H_2/Cl_2 reaction. The function of a heterogeneous catalyst is to alter the energy profile along the reaction path to accelerate the rate of formation of products. For gas phase reactants and products the overall exothermicity cannot be affected by the catalyst. But such catalysts alter reaction rates drastically by altering the energetics of intermediate reaction states. Therefore, from atom-diatom collisions in the gas phase we know the importance of details in the energy path for determining final state populations and can ask, how will a catalyst affect these final state population distributions? Clearly, there must be an effect since the energy profile along the reaction contour changes, but what can be expected in detail? Following what was done for gas phase chemical lasers, we chose to use classical trajectories to attempt to elucidate these features in the gas-solid interaction, most likely to lead to population inversions. Don Bunker was one of the pioneers in classical trajectory methods and would not be surprised to find the method applicable, essentially unchanged, to the emerging area of dynamics of heterogeneous catalysis.

In this paper, we present some recent results concerning chemical dynamics at the gas-solid interface via classical trajectories. This represents the culmination of a series of papers whose goal was to assess the possibility of obtaining vibrational population inversion by means of a heterogeneous chemical reaction. Therefore, in addition to reporting our recent results concerning the dynamics of adsorption, we will provide an overview and rationale for the recent work in this area.

In order to model realistic chemical dynamics, a reasonable model potential is needed. We used a modified 4-atom London-Eyring-Polanyi-Sato (LEPS) model potential to account for the interaction of a diatomic molecule with a solid surface.[9] In our first studies,[10] the surface was assumed to be rigid and provide simply a substrate upon which the reaction could occur. This is consistent with the simplest picture of a catalyst as providing merely a lower-energy pathway from reactants to products but (as a rigid surface) not adding or removing energy from the reaction. A very similar model potential was developed independently by Gelb and Cardillo[11] and used to investigate isotope effects for hydrogen, and cluster formations on a copper surface.[12]

Consistent with the rigid-surface model, we have assumed that the reaction energy to be partitioned in the product molecules must come entirely from the reactants rather than from the substrate. For efficient population inversion to occur, considerable energy must be available. Since catalysts are typically heavy metals, one does not expect a very efficient heat transfer between the surface and rapidly reacting molecules on the surface as an intermediate state in a fast reaction. Therefore, the source of the reaction exothermicity is assumed to be the reaction itself and the surface plays a minor

role dynamically (but a major role in altering the energetics of the reaction path). This assumption has been tested numerically and found to be accurate to ~10%.[13] As discussed above, experimental results have appeared in which the fractional energy deposited in the solid has been measured. While the experiments are not precisely comparable with the present calculations, the data clearly shows that strong chemical bonds are frequently formed without significant energy transfer to the solid.[1,2]

Section II provides a description of our model for chemical dynamics at the gas-solid interface, emphasizing the possibility of obtaining vibrational population inversions from such a system. Section III discusses our most recent results for the dynamics of adsorption as related to the possibilities of obtaining vibrational population inversions and connects these with previous results for the dynamics of heterogeneous recombination. Conclusions are drawn and the possibility of heterogeneously catalyzed reactions leading to useful population inversions are discussed in Section IV.

II. Description of the Model

We envision studying a reaction of the general form

$$A_2 + B_2 \xrightarrow{\text{(gas phase)}} 2AB(V,J) \qquad (1a)$$

$$A_2 + B_2 \xrightarrow[\text{(catalyst)}]{} 2AB(V',J') \qquad (1b)$$

In practice, the direct reaction (1a) frequently has a substantial activation barrier and correspondingly slow rate. The catalyst is chosen specifically to remedy this situation but, by altering the energy contours between reactants and products the (V,J) distributions will also change. Conceptually, it is convenient to discuss the catalytic reaction (1b) in two steps. In the first step, a diatomic molecule (A_2 or B_2) collides with the solid surface and dissociatively chemisorbs. In the second step, the adsorbed atoms A and B encounter one another on the surface and desorb as AB. We do not consider the case in which a gas phase species adsorbs as an undissociated diatomic molecule and this species, rather than chemisorbed atoms, participate in the reaction. Nor do we consider direct reactions between gas phase A_2 and adsorbed B atoms (or the inverse). Both of these cases (particularly the second) could be important for practical catalytic systems operating at high pressure. However, the additional complications introduced into the reaction path by having to follow more atoms materially increase the computational effort. Since our understanding of the dynamics is rather crude, we

believe it is justified to study the simplest realistic system. Hence, we consider reaction (1b) to proceed via dissociative chemisorption of both A and B, a subsequent encounter of the adatoms on the surface, and finally, the desorption of AB. Such a model would be appropriate at low pressures and low coverages of adsorbed species and (obviously) for a system in which A_2 and B_2 do dissociatively chemisorb. In summary, our 2-step process is

$$A_2,B_2\ (\text{gas}) \xrightarrow[\text{Step I}]{} A,B\ (\text{chemisorbed atoms}) \xrightarrow[\text{Step II}]{} AB(V,J),\ (\text{gas}) \qquad (2)$$

The requirement that dissociative chemisorption takes place means Step I should be exothermic for both A_2 and B_2. As argued above, we require AB to receive its internal energy from the overall reaction exothermicity, rather than from the catalyst. Therefore, we have the further restriction that the overall reaction I + II be exothermic. The detailed procedure for modeling the overall reactions I and II is as follows:

Step I: A single diatomic molecule (either A_2 or B_2, for simplicity we will assume A_2) collides with the surface of the solid. Energy may be exchanged with the solid, the A_2 bond may break, or the molecule may rebound into the gas phase. This calculation involves just one diatomic molecule colliding with a moving surface and is well within the computer technology developed previously. This part of the calculation provides estimates of: the efficiency with which dissociative chemisorption occurs, the distribution of kinetic energies for the atoms adsorbed on the surface, and the relative

fraction of energy transferred into the solid (and thus lost to the reaction). All are calculated for a variety of potential surfaces constructed consistent with our assumptions (i.e., exothermic for Step I).

Step II: Two adsorbed atoms A,B encounter each other on the surface, recombine and from a gas-phase diatomic molecule. Again, we must consider only two atoms interacting with a moving surface to compute the state distribution of the products and the energy lost to the solid. The only direct connection between Step I and Step II is through the distribution of kinetic energies of adsorbed atoms on the surface. However, judging from gas phase dynamics, the formation of vibrationally excited product molecules seems to be more sensitive to the energy profile of the reaction contour in the formation step rather than to the detailed initial conditions of the reactants. That is, for an exothermic reaction A + (B,C) the product state distribution is largely determined by the energy profile along the reaction path, and effects due to the initial state of the (B,C) or due to the kinetic energy of collision are not as important.[14]

To this approximation, Steps I and II can be decoupled and computed separately. Detailed studies of recombination dynamics (Step II) have already appeared[13a] and will be briefly summarized below. In this paper we report computational results for the adsorption step (I).

III. Results and Discussion: Dynamics

As indicated, there were reasons to feel that Step II, the recombination step, would be the most crucial in determining the population distribution of the final molecules. Therefore, this step was studied first and in some detail.[13a] We briefly summarize the results here. Using a model potential based on the London-Eyring-Polanyi-Sato (LEPS) method, nine potential surfaces were generated (Figures 1, 2). The original rigid-surface model was generalized to allow for motion of the surface atoms, and, hence, gas-solid energy exchange. Three of the 9 surfaces were endothermic for recombination (Number I, II, III), while the remaining 6 were exothermic for recombination. Various barriers and modes of energy release (early, late) were included. The results for the 9 surfaces are summarized in Tables I and II. The 3 endothermic surfaces did not lead to efficient recombination nor to significant reaction energy appearing in vibration even though kinetic energy considerably in excess of the minimum was supplied. Hence, one requirement for efficient energy deposition in AB seems to be: although A_2, B_2 dissociatively chemisorb on the material, AB should <u>not</u> dissociatively chemisorb (i.e., AB recombination in the surface should be exothermic). This should be a useful guide in choosing candidate systems for experimental studies. We see that some of the systems studied (i.e., VII), produce vibrational population inversions, quite comparable to the HF laser. Also, system VII has a satisfactory amount of energy in $V \geq 2$, which is another important characteristic. Unfortunately, the best results were obtained for the case of equal mass which is likely to be a homonuclear molecule not suitable for IR emissions (although CO could approximately qualify).

In summary, the results for the recombination seem to indicate a good population inversion may be obtained if: (1) the recombination is exothermic, (2) atoms have roughly equal masses, and (3) from potential VII, the energy is released early in the recombination with no barrier to recombination. That vibrational excitation is produced more readily by an attractive potential (i.e., VII), is consistent with the work of Polanyi[14] on gas phase A + BC collisions.

It remains to examine the adsorption step to see if significant energy loss to the surface occurs. We have shown in previous studies that adsorption will proceed efficiently even without energy transferred to the solid if it is exothermic and does not encounter an activation barrier.[10c] Also, we do not expect the detailed motion of the atoms A and B across the surface to be as important as the potential in determining the final state distribution of AB product molecules. Therefore, our chief concern is with the energy transferred to the solid during adsorption and whether or not such energy transfer could be a serious loss of energy otherwise available for AB excitation. We have previously studied the energy transfer for H_2, and HD colliding with a tungsten surface using a potential that had a barrier to adsorption.[10] Here, we report results for a few potentials lacking such activation barriers, as well as for some heavier particles with early and late energy release, and for heavier gas molecules. Potentials 1-3 in Figures 1 and 2 are exothermic to adsorption (endothermic to recombination), provide both early and late energy release, and these were used for our study. Both light and heavy mass combinations were used (to simulate H_2 and a system with the mass of Br_2 colliding with tungsten) and the results are reported to Table III. Both

isolated diatomic molecules were described by a Morse curve with potential parameters given previously.[9] This potential was chosen to reproduce the properties of the isolated H_2 molecule and only the mass was increased to 80 amu to mimic a heavy molecule colliding with the surface. Hence, the system labeled "Br_2" has only the mass of "Br" and the other properties of dissociation energy, force constant, and equilibrium separation appropriate for H_2. The Morse parameters for the isolated diatomic molecule affect the LEPS potential in a complicated, non-linear way.[9-11] Hence, attempting to change the Morse parameters to model more closely a physical Br_2 molecule, would change the total potential and the energetics of the reaction. We believe it is more important to produce a comparison on the same potential with simply a heavier molecule.

Both vibrational and rotation were included. Approximately 1.75 eV of vibrational energy is present in both systems (H_2(V=3), "Br_2"(V=31)). Similarly, the rotational quantum numbers were selected such that equivalent rotational energy (0.09 eV) was present for both molecules. For all cases studied, 9 surface atoms were permitted to oscillate about their lattice sites, according to the Einstein model discussed previously.[13a] The parameters for this oscillation about the lattice are the same as those used in the recombination study of reference 13a.

E_{TOT} in Table III is the total energy available to be depositied into the solid; adsorption energies plus kinetic and internal energies of the gas molecule. The surface temperature was initially 300°K. The energy gained by the solid because of this adsorption is ΔE_s. It is calculated by summing the kinetic and potential energies of the solid atoms as they move about their lattice sites. This is not a precisely defined number because the couplings between the

the surface atoms and adsorbed atoms will cause energy to flow back and forth until the adsorbed atoms recombine and leave the surface, or the adsorbed atoms leave the region of moving surface atoms. In this case, the trajectories were followed until the final separation of the adsorbed atoms exceeded the region of moving surface atoms.

From Table III we see that the larger mass will increase the energy transfer by roughly a factor of 2-3 although the mass increases by a factor of 80. For the worst cases, the energy transfer is approximately 10% of the total energy. However, there are recent indications that the Einstein model used here tends to underestimate energy transferred to the solid when compared with generalized Langevin (GL) computations.[15] The GL computations considered only one moving surface atom, and it is not clear how much this affected the results. That is, several Einstein oscillators may provide a closer approximation to a more accurate GL model (there being more degrees of freedom in the solid in which to store energy) than a single oscillator would provide to a single oscillator GL model. Until these calculations are performed, the results must remain somewhat uncertain. To be conservative, $\Delta E_s/E_{TOT}$ in Table III could be too small by a factor of 2. For H_2 + W(001) the net energy loss to the solid is still within the original estimate of 10%. However, for the mass 80 system, 20-25% energy loss could occur.

V. Conclusion

In conclusion, the current series of computer simulations indicates that vibrational excitation should be possible for heterogeneous reactions. The conditions seem to be that both steps in the reaction, dissociative chemisorption and recombination, should be exothermic. Efficient population inversion occurs for early energy release in the recombination step and for nearly equal mass atoms. A question that has not been fully explored is the energy loss to the solid for all conditions of interest. The present computations indicate that this could be a serious loss (i.e., ~20%) for heavy systems, but should be quite tolerable for light gases. There are indications that heating the substrate would tend to reduce the net energy loss into the solid.[15]

One is tempted to speculate about the possibility of constructing a "catalytic chemical laser" given the estimates of population inversions given above. However, this endeavor is not likely to be fruitful at this stage because there is simply too little data, either experimental or theoretical, with which to do a realistic estimate. The present research indicates that a vibrational population inversion should be possible in reactions catalyzed by a solid surface. There are also indications[16] that collisions of vibrationally excited molecules with surfaces do not invariably lead to deactivation. Deactivation probabilities as low as 10^{-4} are not uncommon. This would be the chief loss mechanism not already present in chemical lasers, and it may be possible to overcome it by an appropriate design. The overriding need now in heterogeneous chemical dynamics appears to be for good measurements of final state population distributions for a variety of prototype systems. If classical

trajectory studies such as these in any way stimulate interest in such measurements, or provide guidance as to how they should be performed, the work and career of Don Bunker in developing the technology must receive due credit.

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FIGURE CAPTIONS

Figure 1 - Equipotential contours (in eV) for the approach of H_2 to W(001) for the different potential surfaces studied. The contour levels are equally spaced for any given potential surface. X indicates the position of the reactants, two atoms adsorbed in adjacent 1CN sites (5CN for IX). • locates our choice of the "transition state." For details of the construction of these surfaces, see Ref. 13a.

Figure 2 - Energy profiles along the reaction paths for the potential surfaces given in Figure 1. The dashed line marks the region of transition from reagents to products (denoted by • in Figure 1). (From Reference 13a.)

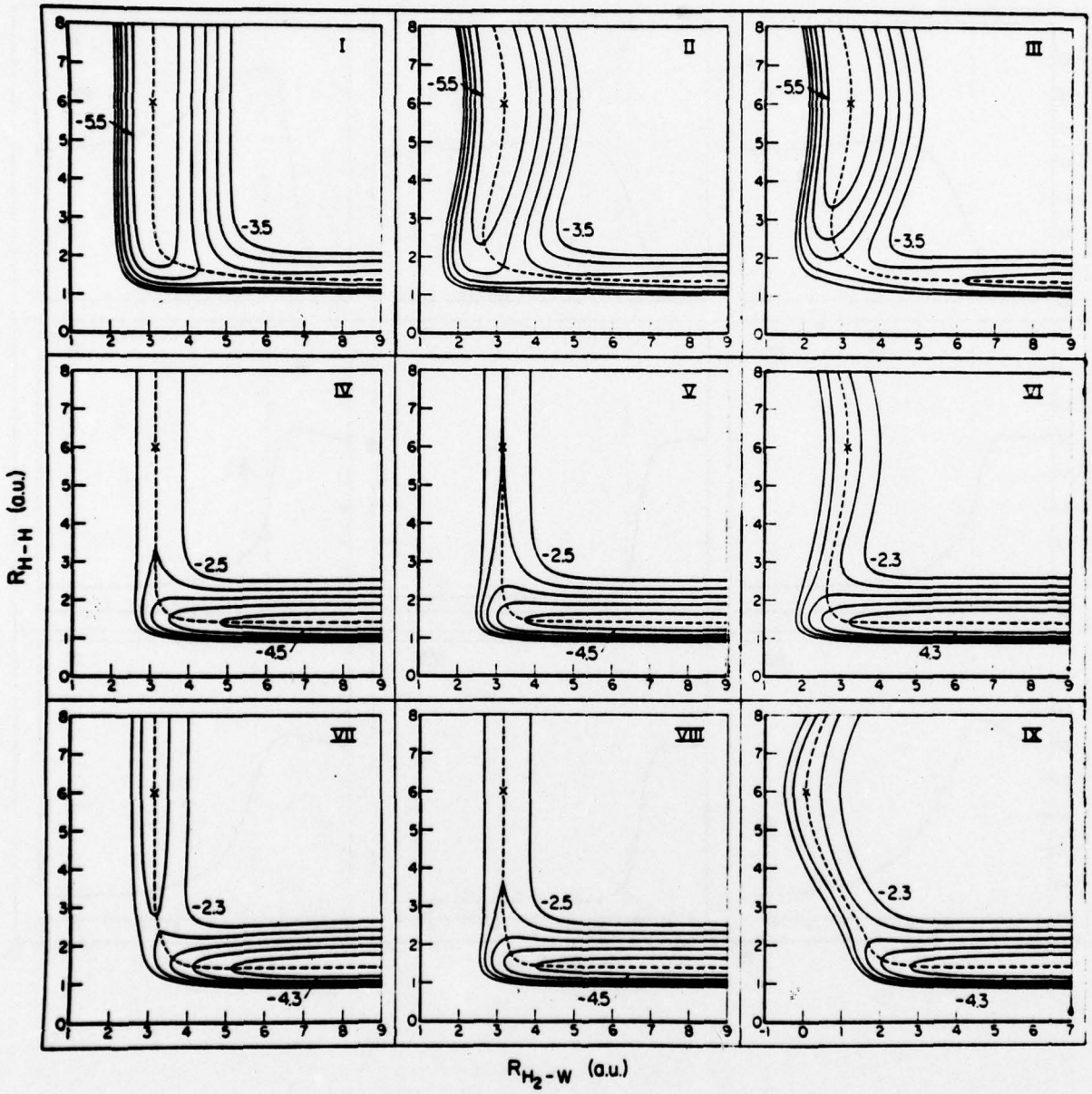


Fig. 1

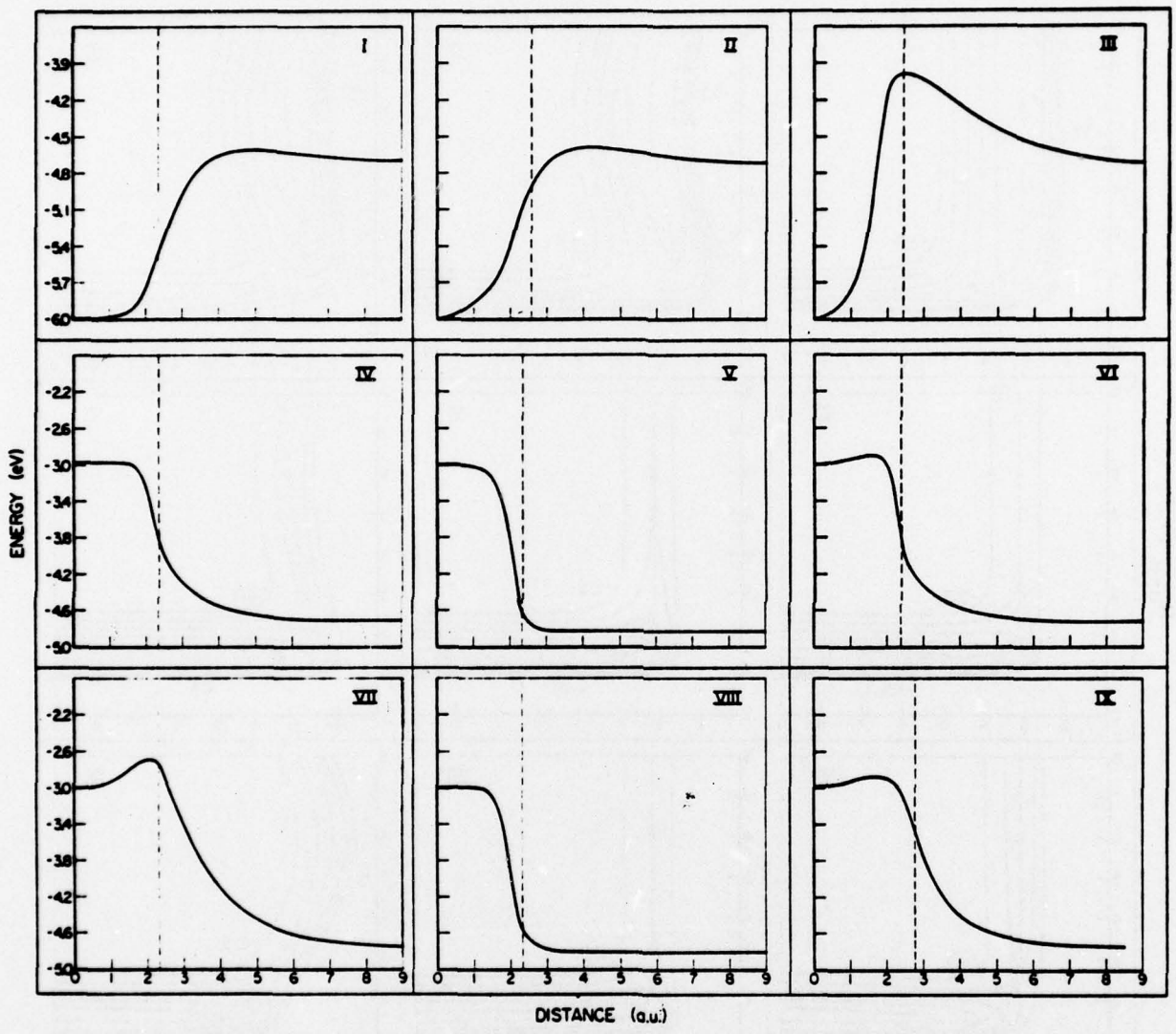


Fig. 2

TABLE I. (From Reference 13a.) Mean distribution of energy in product molecules: (a) rigid surface; (b) two surface atoms free to move.

Potential		% Molecule formation	% E_{vib}	% E_{rot}	% E_{trans}	% Energy Transfer
			(a) Equal masses			
IV	(a)	41	41	15	44	
	(b)	72	49	11	34	6.32
V	(a)	36	60	20	20	
	(b)	78	52	26	15	6.69
VI	(a)	42	51	10	39	
	(b)	65	57	8	30	5.24
VIII	(a)	30	68	18	14	
	(b)	69	62	18	13	7.04
			(b) Light-heavy mass combination			
IV	(a)	21	47	13	40	
	(b)	73	51	10	34	4.79
V	(a)	40	49	30	21	
	(b)	79	37	40	19	3.86
VI	(a)	40	51	13	36	
	(b)	69	47	17	32	5.89
VIII	(a)	26	37	40	23	
	(b)	70	46	27	23	4.26

TABLE II. (From Reference 13a.) Product vibrational state distribution (%) summed over rotational sublevels.

Potential	v = 0	1	2	3	4	5
(a) Equal masses						
IV	18	39	30	12	1	0
V	11	17	36	34	3	0
VI	8	36	39	15	2	0
VIII	1	20	48	26	5	0
IX	14	29	32	24	1	0
(b) Light-heavy mass combination						
IV	11	20	20	30	15	4
V	15	21	26	22	7	9
VI	10	10	23	23	25	10
VIII	18	23	13	13	27	8
IX	39	22	14	20	3	2

TABLE III. Energy lost to the solid for potentials I, II, III defined in Figures 1, 2.

Potential Surface		E_{rel}(eV)	V	J	$\Delta E_s/E_{TOT}$ (%)
H_2 + W(001)	I	0.3	0	0	3.2
	I	0.3	3	0	1.6
	I	0.3	0	3	2.9
	II	0.3	0	0	4.5
	II	0.3	3	0	2.3
	II	0.3	0	3	4.3
	III	0.9	0	0	3.0
	III	0.9	3	0	2.3
	III	0.9	0	3	2.9
	III	0.3	3	0	1.9
	III	0.5	3	0	2.4
"Br_2"+W(001)	I	0.3	0	0	6.2
	I	0.3	31	0	5.0
	I	0.3	0	30	7.0
	II	0.3	0	0	10.2
	II	0.3	31	0	13.1
	II	0.3	0	30	10.6
	III	0.9	0	0	6.5
	III	0.9	31	0	10.3
	III	0.9	0	30	8.4

APPENDIX C

"THE ENERGETICS OF DIATOM/SOLID DISSOCIATIVE ADSORPTION"

THE ENERGETICS OF DIATOM/SOLID DISSOCIATIVE ADSORPTION

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ABSTRACT

The generalized Langevin method for gas-solid scattering is combined with a LONDON-EYRING-POLANYI-SATO type potential function in order to allow calculation of collisions and simple reactions at the gas-solid interface. Energy transfer and dissociative adsorption for selected collision configurations for a diatomic molecule scattering off a Cu (100) single crystal face have been studied by integrating the classical trajectories. Special emphasis is placed on determining the relative importance of the microscopic parameters of the collision system on the microscopic mechanisms of these processes. Energy accommodation and dissociative adsorption were found to be greatly effected by the Debye temperature of the solid.

I. INTRODUCTION

Previously, the many-body nature of gas/solid processes has prevented the theorist from developing a realistic dynamical picture of gas/solid collisions.[1] The recent development of the generalized Langevin method for gas/solid processes reduces this many-body problem to a computationally practical few body problem.[2,3,4] The generalized Langevin theory is based on a few key ideas. Since the impinging gas molecule interacts strongly with only a few of the solid atoms, the dynamics of these solid atoms must be explicitly accounted for. For the collision processes of interest, the motion of the remainder of the lattice is observable only by its influence on the region of strong interaction. Therefore, one need not explicitly follow the detailed motion of the surrounding lattice as long as a sufficiently large region of strong interaction has been included. The surrounding lattice enters the dynamics via friction kernels and random forces. The many-body problem also manifests itself in the diatom-solid surface potential energy problem. This problem has been cast into a computationally tractable form by the use of a London-Erying-Polanyi-Sato type potential function developed by McCreery and Wolken.[5] Combining this potential function method with the generalized Langevin method, we present calculations of collisions and simple reactions at the gas/solid interface in which both chemically realistic model potentials and a treatment of the full lattice dynamics has been included. As a simple example of a chemical reaction, we choose the dissociative adsorption of a diatomic molecule on the (100) single crystal face of copper. Also, the energy transfer occurring during the scattering of diatomic molecule for a solid is investigated via collision configurations arbitrarily constrained to be non-reactive.

This paper is intended to be a preliminary study of the dynamics of diatomic molecule/solid reactive processes with particular attention to the lattice effects. Therefore, we have approximated the directly struck zone (primary zone) of the surface by one moving solid atom. This solid atom was further confined to oscillate perpendicularly to the surface plane. Also, the center of mass of the diatom perpendicularly approaches the moving solid atom in all our trajectories. Only broadside and perpendicular collision configurations were used for the approach of the bond of the diatom. Such configurations greatly simplify the elucidation of the microscopic mechanisms involved.

In this study, we wish to gain a better understanding of how the microscopic parameters of the collision system affect the microscopic mechanisms of gas/solid processes in which chemical reactions occur. In the scattering of atoms from solid surfaces, the duration of the collision is known to determine the extent of participation of many body dynamics in energy accommodation.[4] At a given beam energy, the more massive the gas atoms the smaller the velocity and the longer the collision time. In the present study, we are able to vary collision times by using fictitiously large gas atom masses. The mass ratio of gas atom to surface atom also affects the extent of energy exchange. Parameters of the solid such as the surface temperature and the Debye temperature of the solid have known effects in gas atom/surface energy accommodation.[4] The relative importance of the parameters of the collision system on diatom/surface collision process is poorly understood due to the possibilities of dissociative chemisorption and the participation of internal molecular modes. The present study addresses these problems.

In Section II, we describe the generalized Langevin equation method along with the specifics of the potential energy surface. In Section III, we discuss our calculations and results.

II. GLE METHOD

The generalized Langevin theory for gas/solid processes and its numerical implementation is extensively discussed elsewhere.[2,3,4] Here, we briefly review only those aspects of the theory pertinent to the specifics of our calculations. The set of generalized Langevin equations[2] (GLE) is

$$\begin{aligned} m_j \ddot{\vec{r}}_j &= -m_j\omega_o^2 \vec{r}_j(t) + \int_o^t m\dot{\vec{\Theta}}_j(t-\tau)\vec{r}_j(\tau)d\tau + \\ &\quad \vec{R}_j(t) - \vec{\nabla}_{r_j} W(\vec{R}_1,\vec{R}_2,\vec{r}_1,\vec{r}_2,\ldots) \\ M_i \ddot{\vec{R}}_i &= -\vec{\nabla}_{R_i} W(\vec{R}_1,\vec{R}_2,\vec{r}_1,\vec{r}_2,\ldots) \end{aligned} \tag{1}$$

$\vec{r}_j$ denotes collectively the coordinates of the atom j in the solid (j = 1, 2,...) while $\vec{R}_i$(i = 1,2) denotes the coordinates of the two atoms comprising the incident gas molecule. The present calculation is for a diatomic molecule incident on a solid surface, but this is not an inherent restriction in the theory. $\dot{\vec{\Theta}}_j$ is the damping kernel accounting for the dissipation of energy from solid atom j to the remainder of the solid. $\vec{R}_j(t)$ is the random force experienced by solid atom j due to interactions with the surrounding solid. In general, m_j, $\dot{\vec{\Theta}}_j$, $\vec{R}_j$ could be different for different atoms in the solid, but this generality is not used in the present calculations as we are attempting to model the collisions of a diatomic gas with a solid of uniform composition. Therefore, the subscripts j will be omitted. For the present calculation, the damping kernel $\Theta(t)$ is approximated by a one-term damped sine function obtained by a numerical fit to a modified bulk Debye

model of the solid which was shown previously to be a reasonable approximation.[4,7] ω_o is the fundamental harmonic frequency of the solid, also within the modified Debye approximation. The random force $\vec{R}(t)$ is assumed to be gaussian and generated by procedures described elsewhere.[8]

W is the potential between the incident diatomic molecule and the solid surface. It was chosen to have the form

$$W = W_4 + \sum_{\substack{\text{moving} \\ \text{solid} \\ \text{atoms}}} (W_{M-S} - W_{M-eq}) \cdot \tag{2}$$

The interaction of the diatomic molecule with a rigid solid surface (frozen lattice) is taken to be a modified 4 Body LONDON-EYRING-POLANYI-SATO (LEPS) type potential function W_4.[5a] To allow for motion of the solid atoms, we add W_{M-S}, a 3-Body LEPS function between the moving solid and the diatom. To avoid overcounting the interaction of the molecule with the rigid surface, we then subtract the value of the 3-Body LEPS at the equilibrium position of the solid atom, $W_{M-S_{eq}}$, and sum over all moving surface atoms analogous to a procedure described in detail elsewhere where W_4 was modified by pairwise additive potentials in contrast to the 3-Body correction used here.[5b]

The application of LEPS potential functions to the interaction of molecular hydrogen with the (100) face of Cu has been described previously by E. Gelb and Cardillo[9] in the form:

$$W_4 = \frac{Q_{AB}}{1+S_{AB}} + \frac{Q_{AC}}{1+S_{AC}} + \frac{Q_{BD}}{1+S_{BD}} - \frac{1}{\sqrt{2}}\left\{\left[\frac{J_{AB}}{1+S_{AB}} - \frac{J_{AC}}{1+S_{AC}}\right]^2 + \left[\frac{J_{AB}}{1+S_{AB}} + \frac{J_{BD}}{1+S_{BD}}\right]^2 + \left[\frac{J_{AC}}{1+S_{AC}} - \frac{J_{BD}}{1+S_{BD}}\right]^2 + 6\,\frac{J_{AC}\,J_{BD}}{(1+S_{AC})(1+S_{BD})}\right\}^{1/2} \tag{3}$$

where

$$
\begin{aligned}
{}^1E_{ij} &= \frac{Q_{ij} + J_{ij}}{1 + S_{ij}} \\
{}^3E_{ij} &= \frac{Q_{ij} - J_{ij}}{1 - S_{ij}}
\end{aligned}
\tag{4}
$$

The hydrogen molecule interactions ${}^1E_{H_2}$ and ${}^3E_{H_2}$ are taken to be the usual Morse and anti-Morse functions respectively, and the hydrogen atom-surface interactions are given by

$$
\begin{aligned}
{}^1E_{H,S} &= D_{H,S}(X_1,Y_1)e^{-\beta_{H,S}(Z_1-Z_1^o)(X_1,Y_1)} \\
&\quad \times \left[e^{-\beta_{H,S}(Z_1-Z_1^o)(X_1,Y_1)} - 2\right] \\
{}^3E_{H,S} &= D_{H,S}(X_1,Y_1)e^{-\beta_{H,S}(Z_1-Z_1^o)(X_1,Y_1)} \\
&\quad \times \left[e^{-\beta_{H,S}(Z_1-Z_1^o)(X_1,Y_1)} + 2\right]
\end{aligned}
\tag{5}
$$

with

$$
D_{H,S}(X_1,Y_1) = D_{CuH}^o\left[1 + \alpha_1 \cos\left(\frac{2\pi X_1}{\ell_1}\right)\right]\left[1 + \alpha_2 \cos\left(\frac{2\pi Y_1}{\ell_2}\right)\right] [(1 + \alpha_1)(1 + \alpha_2)]^{-1} \tag{6}
$$

and

$$
Z_1^o(X_1,Y_1) = Z_{CuH}^o\left[1 - \gamma_1 \cos\left(\frac{2\pi X_1}{\ell_1}\right)\right]\left[1 - \gamma_2 \cos\left(\frac{2\pi Y_1}{\ell_2}\right)\right].
$$

The hydrogen-copper potential parameters: D_{H_2}, β_{H_2}, r_{eqH_2}, $D_{H\text{-}Cu}$, $\beta_{H,Cu}$, Z_{CuH}^o, ℓ, S_{ij}, γ_i, and α_i; are given in tables I and II of reference 9. This potential has a minimum energy for dissociation of 7.0 Kcal/mole and a barrier to diffusion of 10 Kcal/mole. The hydrogen-copper potential parameters for

the 3-Body LEPS potential were chosen to be those of Gregory et al[10], and they are given in table I.

III. CALCULATIONS AND RESULTS

Energy exchange and dissociative adsorption have been studied for a diatomic molecule colliding with a solid surface by integrating classical trajectories for the potential function described here, approximating H_2 + Cu(100). Since our primary interest is in understanding what microscopic parameters most sensitively effect gas/solid collision processes, we vary these parameters to elucidate their effect.

(A) ENERGY EXCHANGE

Energy exchange with the surface was studied by colliding a diatomic molecule with the solid restricting the bond axis of the molecule to be perpendicular to the plane of the surface, and positioning the incoming molecule directly over the struck solid atom. For diatom internuclear distances close to the equilibruum distance, this collision configuration is repulsive, and thus no dissociative adsorption should occur for the energies studied here. The purpose of restricting the collision configuration is to remove several complications such as multiple collisions with the surface and diatom rotational dynamics. The internal energy of the diatom was chosen to be the same as that of the ground vibrational and rotational state of the hydrogen molecule, and the kinetic energy of the diatoms center of mass was selected to be 10 Kcal/mole.[11] This value was selected to simulate the experimental conditions of Balooch et al.[6] The temperature of the solid in their experiments was 850°K. Sets of 100 trajectories were run for each set of solid/beam conditions.

The energy loss of a beam of structureless gas particles colliding with a solid is expected to decrease with increasing solid temperature.[4] This was conducted for a molecule with internal vibrational structure by running sets of 100 trajectories for the solid at temperatures of 0°K, 300°K, and 850°K. The diatom was a fictitious hydrogen molecule which was composed of atoms 20 times as massive as a hydrogen atom. We shall call this molecule H(20). The results are shown in Fig. 1, and as expected, average energy transfer does decrease with increasing solid temperature. It is very interesting to note that these collisions were vibrationally adiabatic; that is, there was no loss of vibrational energy by the diatomic molecule. This seems to be the result of the large amount of zero point vibrational energy present in the hydrogen. The extent of the many body effect on energy exchange may be determined by removing the damping kernel and random force from the equations of motion. This model is called the single oscillator or "Einstein" model and the results are also shown in Fig. 1. The average energy exchange is decreased by a factor of roughly 2 although the trend is remarkably well duplicated.

If one varies the Debye temperature of the solid, one effectively varies the primary spring constant and the scaled time for energy dissipation into the solid. This is due to the scaling of the constants in the damping kernel by the Debye frequency and that the primary frequency $\omega_o = \sqrt{.6}\,\omega_D$. One obtains ω_o from the Debye temperature of the solid.[4] As one increases the Debye temperature one increases the stiffness of the spring which should decrease the average amount of energy transferred from the molecular beam. However, an increased Debye temperature also means a quicker dissipation of energy into the solid. We have tested the effect of increasing the Debye temperature of the solid by running sets of trajectories for the model H_2-Cu system where

the surface Debye temperature was set at 100°K, 236°K, and 350°K. Again, the diatom was H(20). The solid's temperature was 300°K. The results of our calculations, see Fig. 2, show that the main effect of increasing the Debye temperature is to decrease the average energy transfer. The single oscillator model results for the average energy transfer were again too small but with the correct trends.

The general trend of increasing gas mass is expected to increase the average energy transfer for cube models.[12] The opposite trend would be predicted by Goodman's driven oscillator models.[13] For a 300°K solid with copper's Debye temperature, we studied the energy transfer of the hydrogen molecule, and fictitious molecules with atoms 10 times and 20 times the mass of hydrogen in H(10) and H(20). We observe that the average energy transfer shows a peak for the fictitious molecule H(10), see Fig. 3. As expected, the hydrogen molecule shows the least amount of energy transfer in the GLE results. The decline in energy transfer for more massive gas molecules is the result of the struck solid atom recoiling and, upon rebound, depositing energy again into the slower moving, more massive molecules. The single oscillator model should converge to the GLE results as one reduces the collision time, i.e. reduces the mass of the diatom at constant kinetic energy. In Fig. 3, we see that the GLE and single oscillator results for the hydrogen molecule are very similar. Only the effect of the random force causes the slight difference in average energy transfer.

(B) DISSOCIATIVE ADSORPTION

We also studied the dissociative adsorption of a diatomic molecule on the (100) single crystal face of copper as a function of solid temperature, Debye temperature of the solid, and gas mass. Again, sets of 100 trajectories were run for each of the different solid/beam conditions. To simplify the

simulation of adsorption, we restrict the configuration of the diatom to be parallel to the surface with the center of mass perpendicularly approaching the oscillating solid atom. The angle a line parallel to the surface makes with the bond axis of the diatom was Monte Carlo averaged with the other initial conditions. This configuration permits the diatom to dissociate upon impact with the surface with its constituent atoms becoming trapped in wells of atomic adsorption. The importance of lattice dynamics on dissociative adsorption becomes immediately obvious in this configuration. This is easily seen by the fact that the rigid surface approximation results in no absorption for any of the three cases of gas mass studied with their internal energy equivalent to the ground vibrational and rotational state of hydrogen.

Experimentally it has been observed that changes in the temperature of the solid will have the largest effect on dissociative adsorption when the dissociation is preceeded by physisorption.[14] Our potential surface does not have a well for physisorption and therefore we expect little temperature effect on our results. The effect of temperature and dissociative adsorption was studied using the fictitious molecule H(20). The GLE curve shows little variation with temperature, see Fig. 4. However, the single oscillator model results are marked by the small probability of adsorption at 0°K. A sample study of the trajectories indicates that this is due to spurious processes. The diatom actually dissociates and the atoms bounce off adjacent solid atoms and recombine. Since the single oscillator model contains all of the energy lost by the colliding molecule, the solid atom is able to kick out the recombined gas molecule. This mechanism occurs in the GLE calculations when the gas atoms bounce back before the surface solid atom can dump its energy into the lattice. Either quickly moving gas atoms such as hydrogen or long Debye periods of the solid bring this about. Therefore, one sees the importance

many body effects have on simple 0°K dissociative adsorption. Another spurious mechanism occurs for finite temperature, single oscillator trajectories. The atoms of the dissociated gas molecule oscillate on the surface in potential wells adjacent to the solid atom with which they collided. The moving solid atom kicks some of these oscillating gas atoms into adjacent wells. Our model contains no energy loss mechanism to the solid when the adsorbed atoms are at such a great distance from the moving solid atom. None of the GLE trajectories tested showed this spurious effect.

Increasing the Debye temperature of the solid has two counterbalancing effects. As one increases the Debye temperature one increases the spring stiffness and therefore decreases the average amount of compression of the metal atom oscillator for the same energy input. When the extent of compression of the solid atom is decreased, the attraction of the atoms of the colliding diatom for atomic adsorption wells is decreased. Also, the atoms of the colliding molecule will have more kinetic energy on the average after collision with a stiffer spring, as was shown by the energy transfer calculations (Fig. 2). The rate of energy dissipation into the solid increases with increasing Debye temperature.

In order to ascertain the combined effect of these factors, we ran reactive trajectories for several Debye temperatures for the fictitious molecule H(20). Our calculations indicate that increasing the Debye temperature of the solid decreases the amount of dissociative adsorption, see Fig. 5. It is interesting to note that several of the GLE trajectories for the Debye temperatures of 100°K and 350° were able to recombine and desorb. The single oscillator model displays no dissociative adsorption for the Debye temperature of 350°K. Without the many body dynamics, the single oscillator model quickly becomes equivalent to the rigid surface results.

As Fig. 6 displays, an increase in the gas mass results in a steady increase in adsorption probability for both the GLE and single oscillator model.

SUMMARY AND CONCLUSION

We have presented calculations of collisions and simple reactions at the gas/solid interface. As a preliminary study of the dynamics, we restricted the collision configurations to remove certain dynamical complications. In this light, we have studied the relative importance of the microscopic parameters of the collision system on the microscopic mechanisms of dissociation and energy accommodation. A large dependence of both energy accommodation and dissociative adsorption on the Debye temperature of the solid was found. An increase in the Debye temperature drastically decreases both the energy transfer and the amount of dissociative adsorption. Energy accommodation was found to decrease with increasing solid temperature; however, dissociative adsorption, which is not preceeded by physisorption, is not affected by this increase. The importance of including the many body nature of the solid was shown through the spurious results of the single oscillator model in the dissociative adsorption studies.

In conclusion, we wish to emphasize that this study is only a start in unraveling the microscopic mechanisms of reactive gas/solid processes. In a more realistic collision model, several surface atoms will be strongly interacting with the incident gas. A further complication of such a study would be the determination of the number of moving surface atoms which must be included. We have started our studies with a more simplified model so as not to obscure the nature of the process.

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TABLE

Table 1. The parameters of the Morse functions which are used in the 3 BODY LEPS for the gas atom-copper atom potential are taken from A. R. Gregory, A. Gelb, and R. Silbey.[10] We modified their more parameter associated with the well width in order to prevent the tunneling of gas atoms into the solid.

Well Depth = 0.316 eV

Well Width = 0.5 a.u.

Equilibrium Internuclear Distance = 2.3 Å

FIGURE CAPTIONS

Figure 1. ΔE vs. temperature of the solid for H(20)/Cu(100) scattering. Error estimates are the usual error in the mean $N^{-1/2}$ (standard derivation) where N is the number of trajectories.

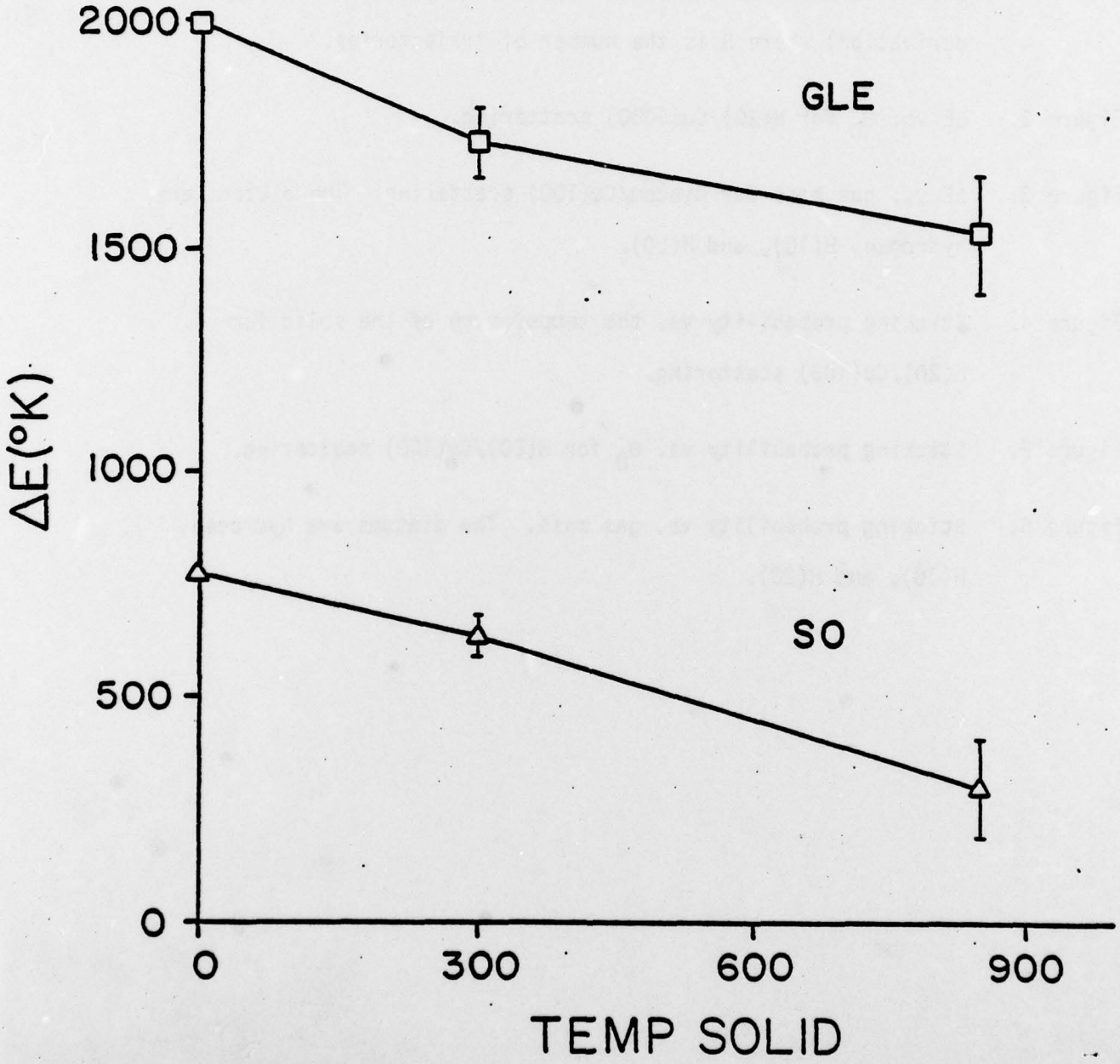
Figure 2. ΔE vs. Θ_D for H(20)/Cu(1000) scattering.

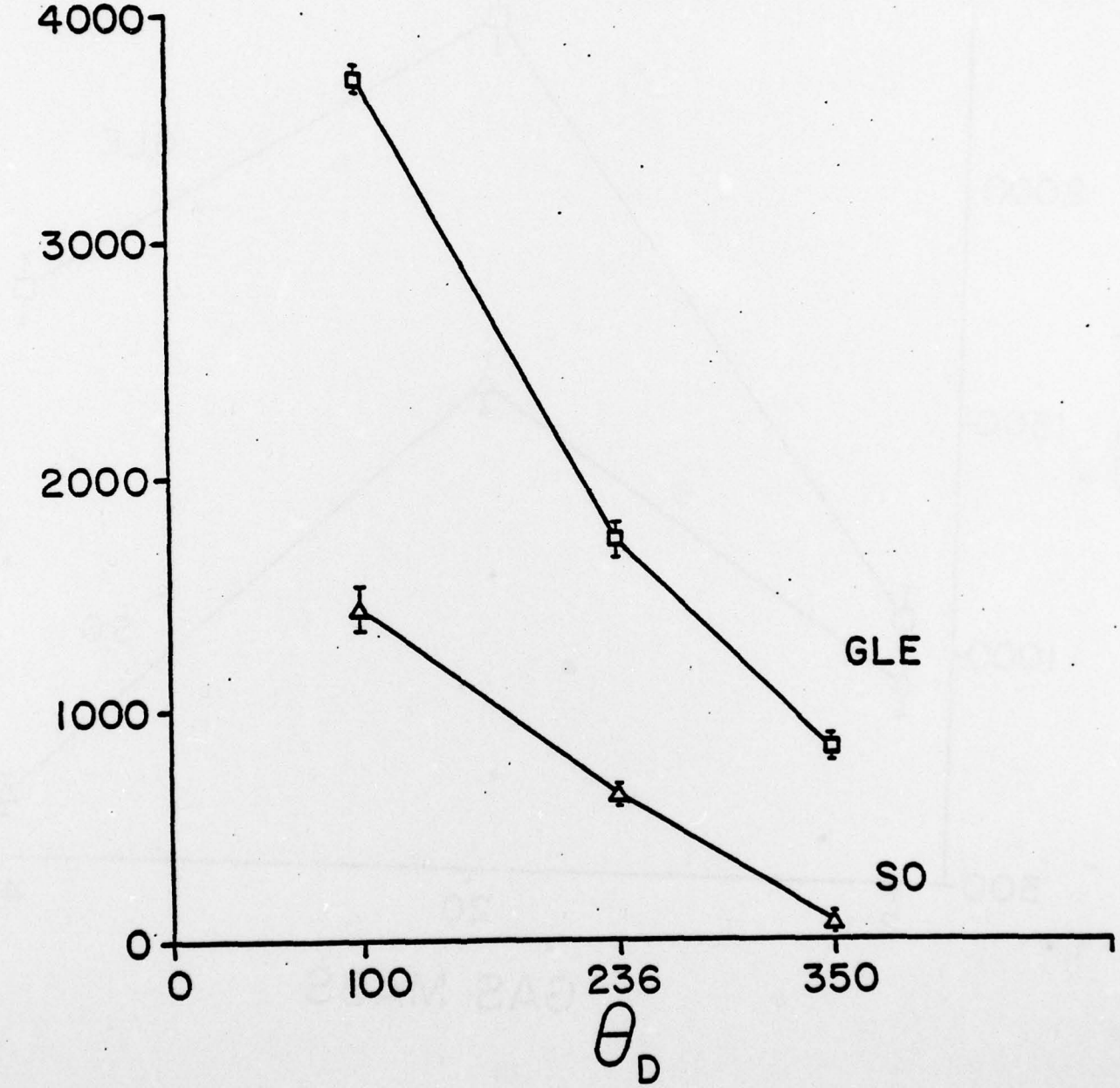
Figure 3. ΔE vs. gas mass for diatom/Cu(100) scattering. The diatoms are hydrogen, H(10), and H(20).

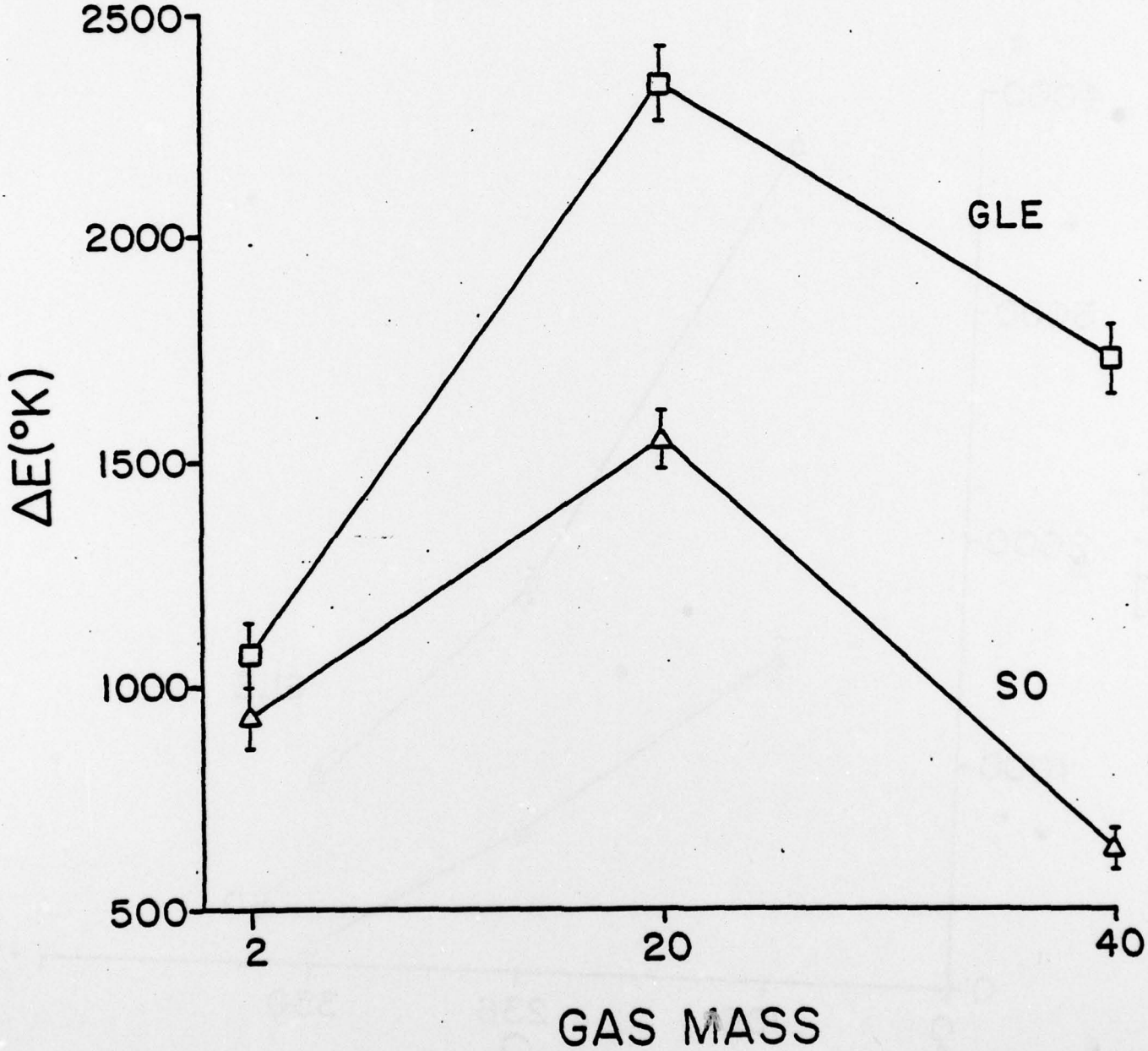
Figure 4. Sticking probability vs. the temperature of the solid for H(20)/Cu(100) scattering.

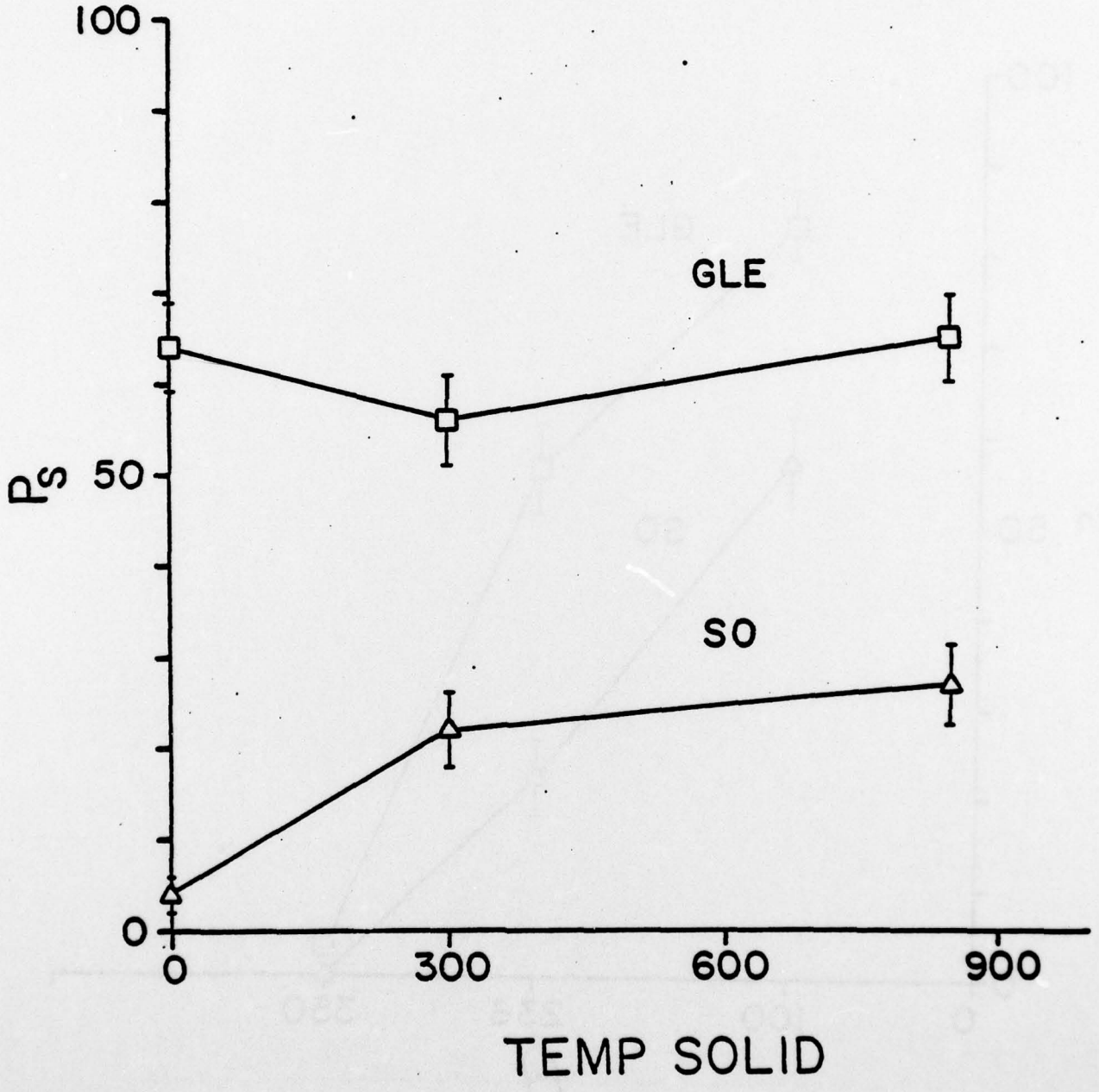
Figure 5. Sticking probability vs. Θ_D for H(20)/Cu(100) scattering.

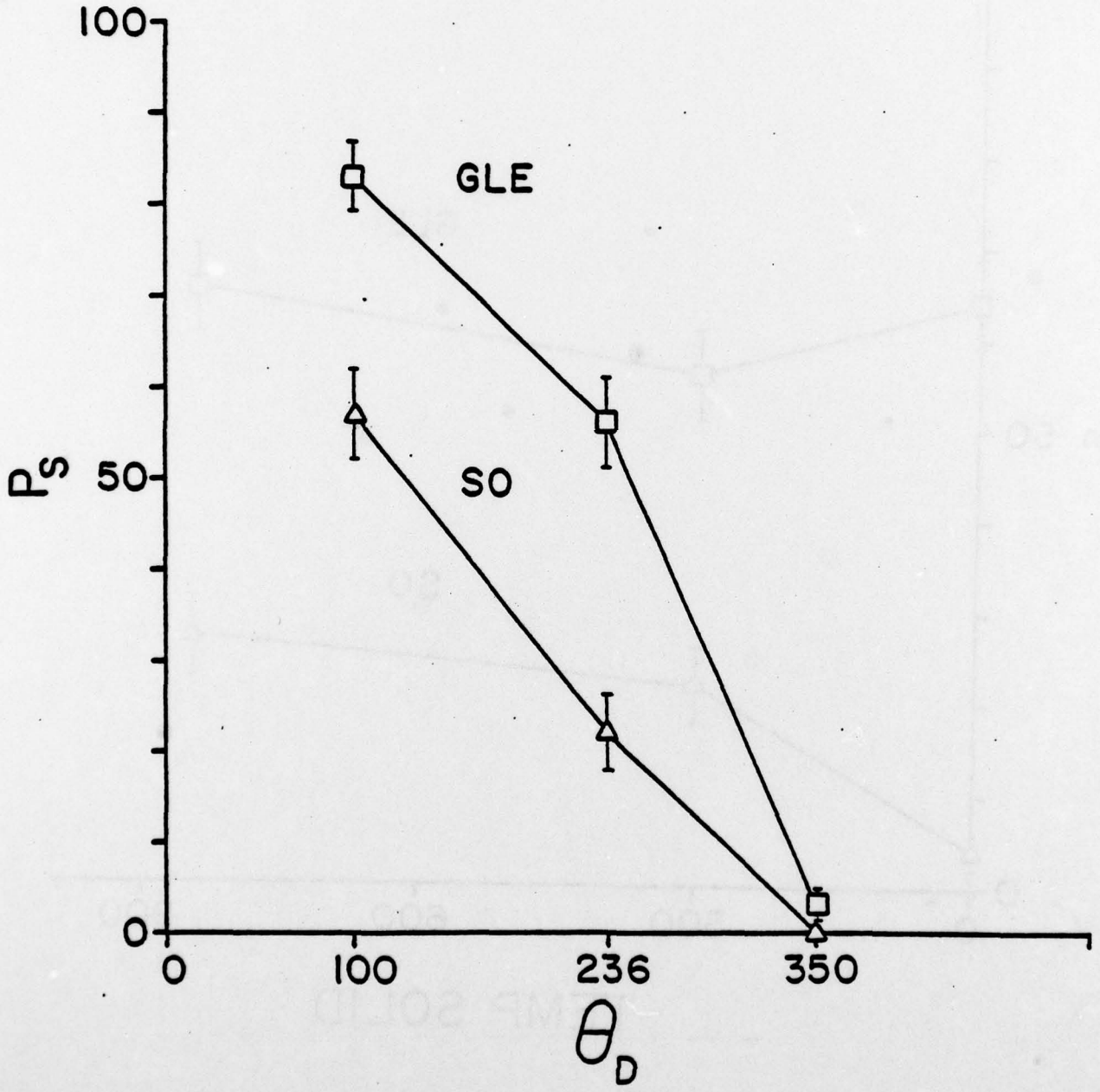
Figure 6. Sticking probability vs. gas mass. The diatoms are hydrogen, H(10), and H(20).

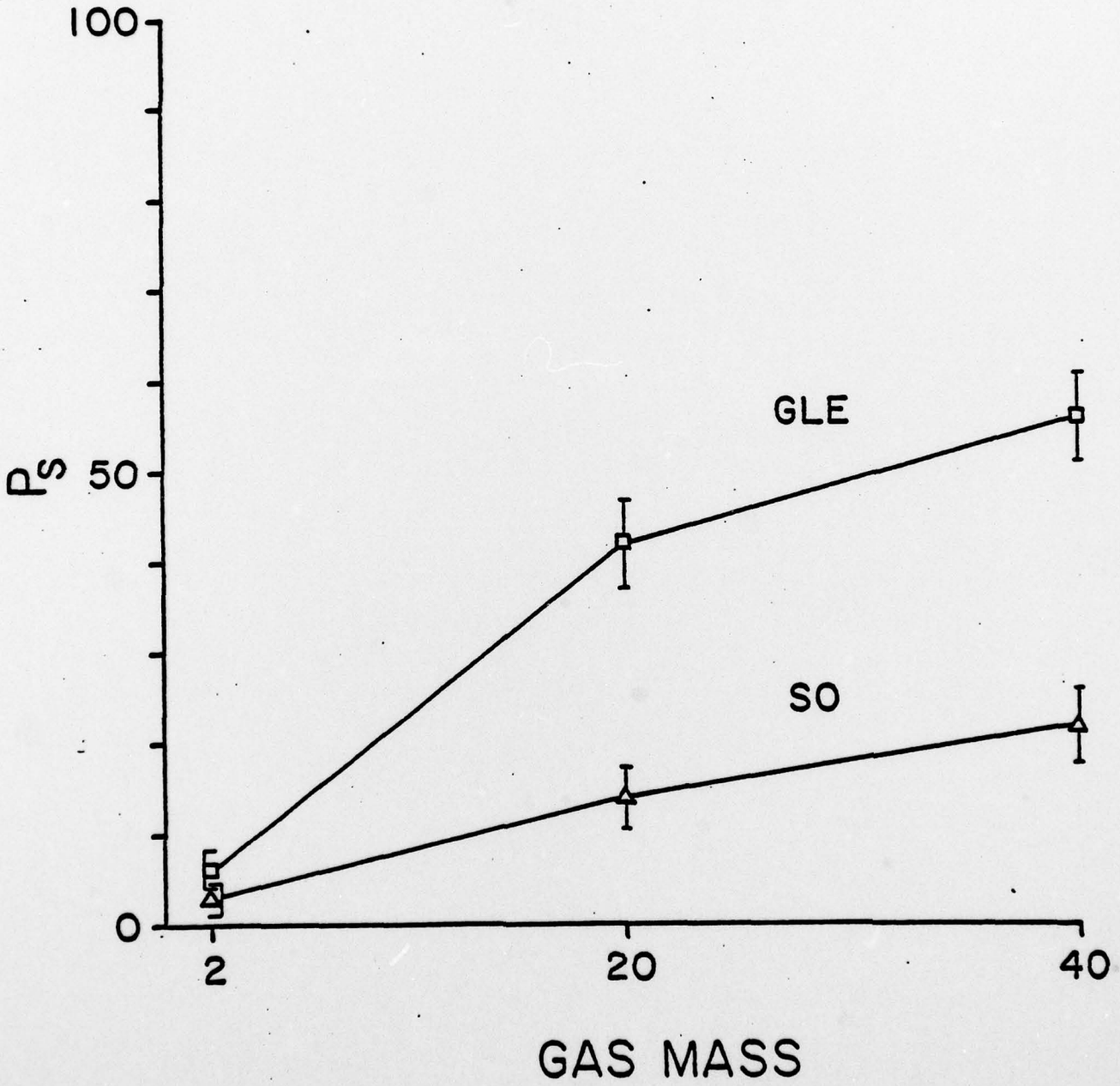

2000
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ΔE(°K)
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TEMP SOLID


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2000
1000
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ΔE(°K)
GLE
SO
0
100
236
350
θD


2500
2000
1500
1000
500
ΔE(°K)
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40
GAS MASS


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GAS MASS