

THEORY OF NEAR-RESONANT CHARGE-EXCHANGE IN GAS-SURFACE REACTIONS

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A theory is presented for describing near-resonant charge-exchange processes occurring in gas-surface collisions. The surface is represented by a cluster of atoms and its electronic properties are obtained from the Diatomics in Molecules procedure. The Polyatomics in Molecules approach is used to calculate the gas-surface interaction potentials and couplings. Trajectories for the transition probabilities and nuclear variables are obtained from the common eikonal formalism. Preliminary results are presented for Na scattering from a W(110) surface. The surface consists of five W atoms. The approach of the sodium atom is perpendicular to the surface and it collides with the center W atom. Generally, it is found that the probability of electron transfer increases with the initial kinetic energy of the sodium atom (5–60 eV) and can attain values larger than 40%.

1. Introduction

In the field of surface science, a variety of experiments are performed in order to obtain information about the electronic and structural properties of the surface. The target can consist of a single component or have particles adsorbed on it. Most of these experiments employ as a probe a beam of particles. The nature of the probe varies considerably in that it can be made up of photons, electrons, neutrons, atoms, ions or molecules. The kinetic energy of the probe also varies from meV up to MeV. The particles that are detected and analyzed in these experiments are either reflected particles from the beam itself or they are secondary particles that result from the interaction of the probe with the target. The mass, kinetic energy, angular distribution, internal state (rotation, vibration, electronic), etc. of the detected particle can in principle be analyzed and all of these measurements provide information about the initial state of the surface.

The theories that have been developed to interpret these experiments are as numerous as the types of experiments themselves. This is in part due to the variety of processes that give rise to the particles being detected. For example, ion neutralization spectrometry [1] experiments measure the energy of secondary electrons produced via Auger processes when the surface neutralizes the incoming ion probe. The energy of the secondary electron is related to the band structure of the surface. The theory developed by Hagstrum [2,3] is based on these Auger processes and gives a description of the phenomenon in terms of the electronic states of the probe (neutral and ionic), the band states, of the

surface, the probability of an electronic transition and the velocity of the probe. An example of a different kind of process is provided by the electron stimulated desorption experiments. These employ as a probe a beam of electrons which cause transitions of particles adsorbed on the surface to excited electronic states. This results in the desorption of adsorbed particles from the surface and the analysis of their energy and angular distribution yields information about the adsorption energy and geometry of the adsorbates. The theory of Menzel, Gomer and Redhead [4] uses Frank-Condon transitions between electronic states to interpret these experiments.

The processes described above are typical of a class of electronic transitions referred to as adiabatic. By adiabatic it is meant that there is little or no exchange of nuclear and electronic energy during the transition process. These processes usually dominate when the energies of the electronic states involved are relatively far apart. This however is not always the case.

The experiments by Erickson and Smith [5] show an oscillatory behavior in the He^+ ion intensity scattered from Pb, Ge, Bi and In surfaces as a function of the kinetic energy of the He^+ ion beam. This type of behavior has also been observed in gas phase ion-molecule scattering [6] and typically occurs when the energy levels of the electronic states involved in the transition lie close to each other in some region of the ion-molecule relative separation. This mechanism of electron transfer is called near-resonant charge-exchange. This mechanism differs from the previous two in that nuclear and electronic energy can be interchanged. In fact, the couplings that cause transitions result from the breakdown of the Born-Oppenheimer approximation and have been termed nonadiabatic couplings. This type of mechanism is responsible for determining the final elec-

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tronic state (ionic, neutral, excited) of the detected particles when a low energy atomic beam whose ionization energy lies close to the conduction band of a metal is scattered from it.

The developments presented here focus on the near-resonant charge-exchange mechanism and are applied to a hyperthermal energy neutral sodium beam scattering off a W(110) surface. This system is chosen partly because it has been observed experimentally [7] that there is a large probability (> 90%) for the sodium atom to be ionized by the surface. Sect. 2 treats the surface electronic problem and constructs the atom-surface interaction potentials and nonadiabatic couplings. In sect. 3., these potentials and couplings are used in a recently developed formalism [8] that predicts transition probabilities. In addition, some preliminary results for the ionization probability for sodium are presented. The paper closes with a discussion in sect. 4.

2. Surface characterization, interaction potentials and couplings

This section treats the electronic part of the problem for the Na-W(110) system. The general concept is to define an electronic problem for the W(110) surface that is solvable and contains no arbitrary parameters. The solutions (eigenvalues and eigenfunctions) of this problem are combined with the solutions of the sodium atom and ion to obtain the Na-W(110) interaction potentials and nonadiabatic couplings. Since the details of this procedure have been presented elsewhere [9,10], only a brief sketch of it and the results are presented here.

The most obvious and physically appealing way to characterize the surface is to use the continuum states and energies corresponding to its valence band. Ideally these could be used along with the incoming atom's electronic states and energies to determine the potentials and couplings. However, from a calculational point of view, it is difficult to obtain these potentials and couplings from first principles if this type of electronic prescription is used. An alternative approach is to approximate the surface with a small metal cluster. This allows the use of well documented electronic structure techniques to determine the electronic energies and states of the surface which results in well defined potentials and couplings for a projectile scattering from the surface. Furthermore, the surface electronic problems can be solved with and without an extra electron present so that incorporating states corresponding to electron transfer presents no difficulty.

In the following, the W(110) surface is represented by a cluster of five tungsten atoms and is shown in fig. 1. The interatomic distances and their relative placements reflect the geometry of the W(110) crystal face. Of the many available schemes (Hartree-Fock, CNDO,

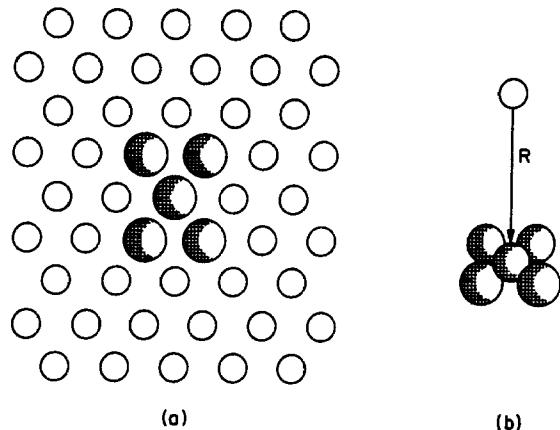


Fig. 1. a) W(110) surface. The five shaded atoms in the middle are used to approximate the surface. The lattice constant is 3.16 Å. b) Trajectory of the sodium atom. It approaches perpendicular to the five atom surface and collides with the central W atom. R is the distance between the sodium atom and the central W atom. (Taken from reference [10].)

Hückel, ...) for solving the electronic problem, the method of Diatomics in Molecules (DIM) [11] seems to be most suitable. This is because the scheme is computationally feasible, it leads to the correct asymptotic products, it has been successfully used for small molecules and it is capable of using whatever experimental or theoretical data is available for the component diatomics. Its use of experimental data for the diatomics makes it a semiempirical method but in some cases this is an advantage because some of the electron correlation energy is included.

Recently a simplified version of the DIM procedure was presented [9] along with a formal treatment of the 5 nuclei, 5-electron (neutral surface) and 5 nuclei, 6 electron (ionic surface) cases. The cluster here meets this prescription if the W atoms are assumed to have one s -like atomic orbital that can be either singly (neutral) or doubly (ionic) occupied. This is undoubtedly an oversimplification but a better electronic description would require more experimental or theoretical data which is not yet available. The information needed here are the valence bond basis functions (see ref. [9] for details) and the ground and first excited state energies for both the W_2 and W_2^- diatomics.

There is considerable uncertainty in what are the energies for W_2 and W_2^- and a full discussion on how these were estimated can be found in ref. [10]. The attractive potentials (ground state) are all chosen to have the form of a Morse potential,

$$V(r) = D(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) + E_0 \quad (1)$$

and the repulsive potentials (first excited state) have the

of a Born–Mayer potential

$$V(r) = A e^{-Br} + E_0. \quad (2)$$

Here E_0 is the sum of the electronic energies of the atoms or ions in the diatomic. The zero of energy corresponds to all atoms being in the ground electronic state, infinity separated and at rest. The constants needed in the potentials for the various diatomics are given in table 1 and the potentials are shown in ref. [10].

The DIM procedure for this system results in fifteen surface eigenvalues and eigenfunctions. Five of these correspond to a neutral surface and the remaining ones correspond to an ionic surface. These eigenvalues along with the C_{2v} symmetry designation of their corresponding eigenfunctions are given in ref. [10].

The Polyatomic in Molecules scheme (PIM) [12] is used to construct the Na–W(110) interaction potentials and couplings. The input needed in this procedure are the eigenvalues and eigenfunctions of the surface, the corresponding ones for the sodium and the interaction potentials between the sodium and surface atoms. Diatomic potentials are needed for NaW, Na^+W and Na^+W^- . These are also given the form of Morse and Born–Mayer potentials with the exception of Na^+W^- . At short range it has the form of a Morse potential and is fit at $r = 2.85 \text{ \AA}$ to a Coulomb potential, i.e.,

$$V(r > 2.85 \text{ \AA}) = -14.4 (\text{eV \AA})/r + 5.12 (\text{eV}) - 0.816 (\text{eV}), \quad (3)$$

where the last two terms are the ionization potential of Na and the electron affinity of W, respectively. These potentials are discussed at length in ref. [10]. The coefficients for these potentials are given in table 1.

The PIM procedure leads to 15 interaction potentials, five of which are asymptotically neutral and ten asymptotically ionic. Choosing the Na trajectory to be

Table 1
Morse parameters

Diatomic	D (eV)	a (\AA^{-1})	r_0 (\AA)	E_0 (eV)
W_2	5.60	1.61	2.20	0.0
W_2^-	2.13	1.61	2.20	-0.860
NaW	1.14	1.04	2.80	0.0
Na^+W	1.56	0.890	2.80	5.12
Na^+W^- ^{a)}	0.88	4.25	2.74	0.0

Born–Mayer parameters

Diatomic	A (eV)	B (\AA^{-1})	E_0 (eV)
W_2	54200	3.50	0.0
W_2^-	54200	3.50	-0.816
NaW	2700	3.64	0.0

^{a)} $r \leq 2.85 \text{ \AA}$, see eq. (3) in text.

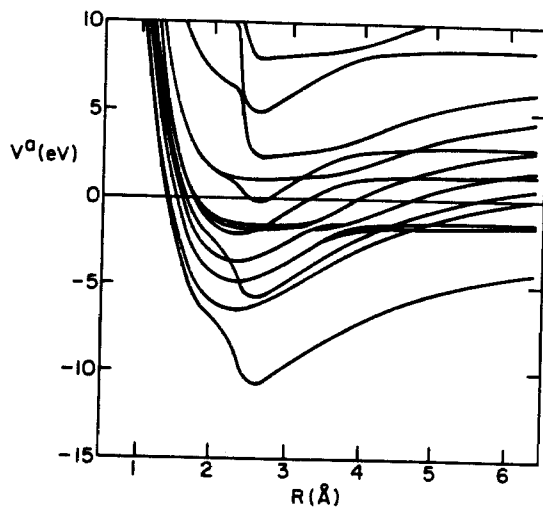


Fig. 2. Adiabatic potentials for the sodium atom interacting with the surface. The Na trajectory and definition of R are given in fig. 1. (Taken from reference [10].)

normal to the surface and aimed at the center W atom (see fig. 1) leads to the potentials shown in fig. 2. Here and in what follows, the positions of the surface atoms are held fixed. The results may seem to be a little complicated but symmetry restrictions somewhat simplify them. Instead of fifteen coupled states, one is left with six A_1 states (four ionic and two neutral) that can couple and three each of A_2 , B_1 and B_2 symmetry (two ionic and one neutral) that can couple.

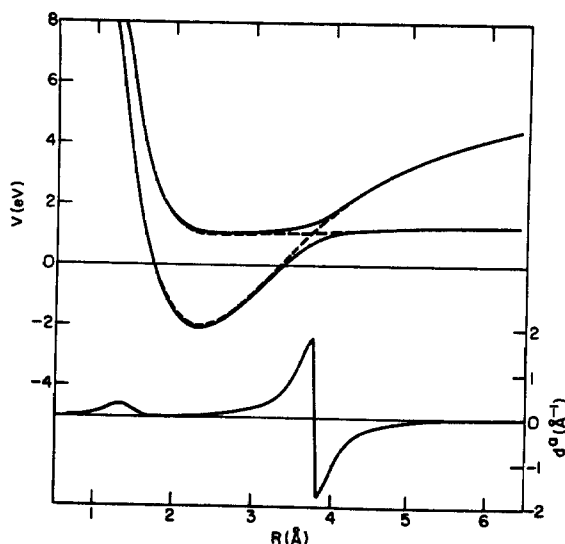


Fig. 3. Adiabatic (—) and diabatic (---) potentials and the nonadiabatic coupling of B_1 symmetry for the sodium atom interacting with the surface. The Na trajectory is given in fig. 1.

The trajectory calculations of the next section use the neutral B_1 state as the initial electronic state of the system. This choice is somewhat arbitrary but it results in a two electronic state problem which is a convenient starting point for this study. The potentials for this symmetry designation along with the coupling

$$d^a = \langle \Psi_2^a \left| \frac{d}{dR} \right| \Psi_1^a \rangle \quad (4)$$

between the upper two states are shown in fig. 3. The superscript a in eq. (4) indicates the adiabatic electronic representation. One notices the avoided crossing at around 4 Å which coincides with the largest magnitudes of the nonadiabatic coupling term. The lowest state (not shown) crosses the neutral state at around 12 Å but the coupling is extremely narrow so that these two states can be treated as noninteracting diabatic states. Thus one is left with a two electronic state problem.

3. Dynamics and results

In this section, a brief discussion of the equations used to obtain the transition probabilities is presented. The details of using this approach can be found in refs. [8,10,13]. The formalism used here is the common eikonal method which has an advantage over other semiclassical treatments in that the trajectories for the nuclear positions and momenta are not assumed but rather coupled to the trajectories for the transition amplitudes.

The formalism originates in the time independent Schrodinger equation. The Hamiltonian for this system with the surface nuclei fixed and the Na trajectory restricted to be aimed toward the central atom is simply

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + \hat{H}_{el}. \quad (5)$$

The matrix representation of the electronic Hamiltonian, \hat{H}_{el} , is chosen to be the diabatic electronic representation [14]. The diabatic representation is related to the adiabatic representation of the previous section by means of a unitary transformation which in turn depends on the integral of the nonadiabatic coupling between the adiabatic states, $|d^a|$. In the diabatic representation, all of the couplings due to the nuclear gradient operator vanish and are replaced by off-diagonal matrix elements of \hat{H}_{el} . The diagonal diabatic matrix elements, designated by the superscript d , of \hat{H}_{el} are shown in fig. 3. One notices that the diagonal terms, $V_{1,1}^d$ and $V_{2,2}^d$, cross in the region where the adiabatic states exhibit an avoided crossing.

In order to add physical insight into the common eikonal approach it is helpful to consider the solutions of eq. (5) in the absence of the potential term, \hat{H}_{el} . In this case, the solutions are proportional to $\exp(iPR/\hbar)$

(traveling waves) and the energy is $P^2/2M$, i.e. kinetic energy. The term PR in the exponential is called the eikonal, S , and one also has that $(dS/dR)^2/2M$ is the kinetic energy of the system. The derivative of the eikonal is just, in this simple case, the momentum, P .

In the more general case considered here, the solutions of the time independent Schrodinger equation satisfy

$$\left(-\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + \mathbf{V}^d \right) \Psi(R) = E\Psi(R), \quad (6)$$

where \mathbf{V}^d is the $n \times n$ diabatic matrix representation of \hat{H}_{el} and Ψ is a $n \times 1$ column matrix. The dimensions of the matrices are related to the number of electronic channels. For the problem treated here, the dimension of \mathbf{V}^d and Ψ are 2×2 and 2×1 , respectively. In the common eikonal treatment, the solutions of eq. (6) are written in the form

$$\Psi(R) = \chi(R) e^{(i/\hbar)S(R)}, \quad (7)$$

where the eikonal, $S(R)$, is common for all electronic channels. Using eq. (7) in eq. (6) and employing the short wavelength approximation, i.e. neglecting terms involving the second derivative of χ , results in a first order differential equation for χ . Without going into detail (see ref. [8]), a transformation into time is made, i.e. $R \rightarrow R(t)$, $dS/dR \rightarrow P(t)$ and $\chi(R) \rightarrow \mathbf{C}(t)$, which gives first order differential equations in time. Defining the Hamiltonian as

$$H = P^2/2M + \bar{V}, \quad (8)$$

where

$$\bar{V} = \mathbf{C}^\dagger \mathbf{V}^d \mathbf{C} \quad (9)$$

leads to $(C_j = (1/\sqrt{2\hbar})(C_j^R + iC_j^I))$

$$\frac{dC_j^R}{dt} = -\frac{\partial H}{\partial C_j^I} \quad (10)$$

and

$$\frac{dC_j^I}{dt} = \frac{\partial H}{\partial C_j^R}. \quad (11)$$

Eqs. (10) and (11) are in the form of Hamilton's equations of motion and furnish a means of determining the transition amplitudes as a function of time. This is a coupled set of equations in that the partial derivatives on the RHS contain terms involving amplitudes from other channels.

One notices from eqs. (8) and (9) that the independent variables in the Hamiltonian are R , P and $\{C_j\}$. Although eqs. (10) and (11) in principle determine C_j , some specification of the trajectories for R and P must be made. If one chooses

$$\frac{dR}{dt} = \frac{\partial H}{\partial P} \quad (12)$$

and

$$\frac{dP}{dt} = -\frac{\partial H}{\partial R} \quad (13)$$

then the total energy of the system is conserved, i.e. $dH/dt = 0$.

Eqs. (10) through (13) form a self-consistent set of coupled equations since their evolution is governed by a common Hamiltonian. We see here a major distinction between other semiclassical treatments and the method used here. In many semiclassical formulations, the amplitudes are coupled to each other but not to the equations of motion for R and P . Here all of these equations are coupled together which makes unnecessary any assumptions about the trajectories for R and P . The price that is paid is that R and P are no longer physical quantities. This is manifested by their dependence on the average potential \bar{V} . This inconvenience is considered small since the main objects of interest in this study are the transition amplitudes.

A typical calculation is done by selecting an initial electronic state (the B_1 neutral state), a value of R sufficiently large so that the sodium surface interaction is negligible, and the initial kinetic energy of the sodium atom which fixes its initial momentum. The equations

of motion are simultaneously integrated until well after the collision is over. Calculations are done for various initial kinetic energies.

The trajectories for R , P and P_i ($P_i = C_i^* C_i$) for an initial kinetic energy of 60 eV are shown in fig. 4. Also shown are plots of \bar{V} and the diagonal elements of \mathbf{V}^d . The results for R vs t indicate that the sodium atom approaches the surface, undergoes a single collision and leaves. P is initially negative and constant, becomes more negative as the sodium atom nears the surface, goes to zero at the turning point and then becomes positive. The increase in the magnitude of P when the sodium is near the surface indicates that it is influenced by the ionic potential V_{11}^d . This influence of V_{11}^d is also seen in the development of \bar{V} during the collision. Initially \bar{V} coincides with V_{22}^d , i.e. the initial electronic state. In the vicinity where V_{11}^d and V_{22}^d cross, \bar{V} decreases and attains a value that is nearer to V_{11}^d hence the increase in $|P|$. On the outward path, the diabatic curves again cross and the final value of \bar{V} lies between those of V_{11}^d and V_{22}^d . That \bar{V} does not equal V_{22}^d means that the probability for being in the ionic state is not zero. The plots of P_1 and P_2 show that there are two regions which coincide with the crossing regions of V_{11}^d and V_{22}^d where the probabilities undergo large changes.

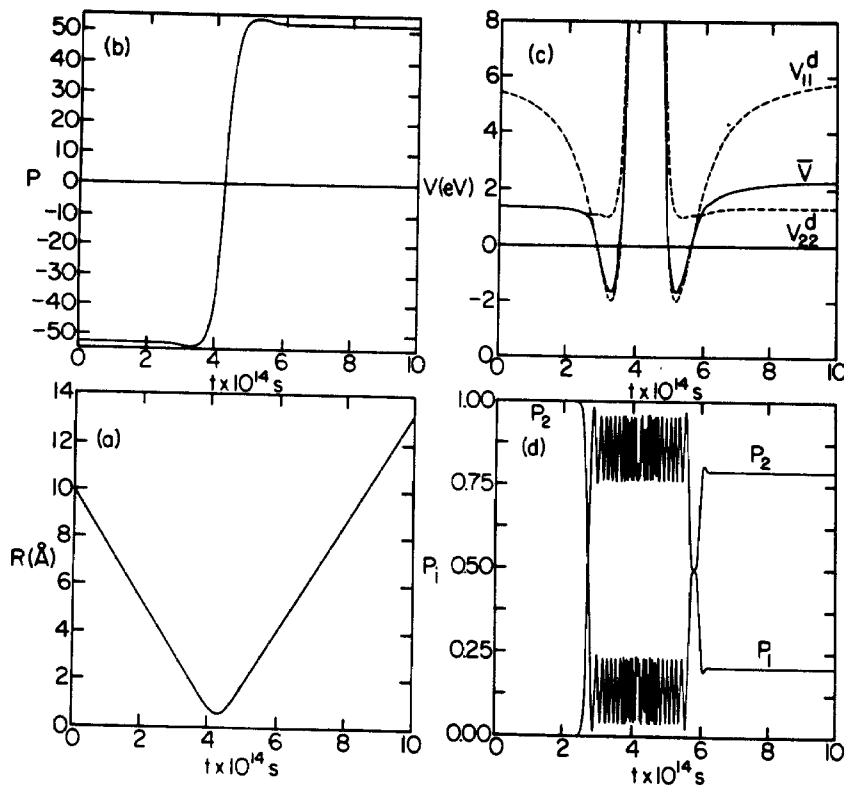


Fig. 4. Trajectory results for an initial kinetic energy of 60 eV. a) R vs t . b) P vs t , the unit of P is 3.8×10^{-17} g cm/s. c) Diabatic potentials, V_{11}^d and V_{22}^d , and \bar{V} vs t . d) P_1 and P_2 vs t . P_1 and P_2 are initially 0 and 1 respectively.

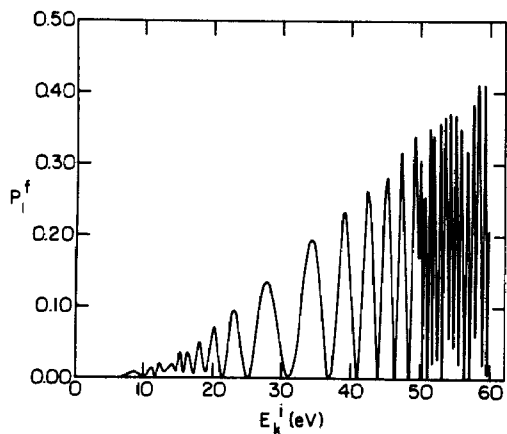


Fig. 5. Final values of the ionization probability, P_i^f , versus the initial kinetic energy, E_k^i , of the sodium atom.

The oscillations between 3 and 6×10^{-14} s are due to the off-diagonal term V_{12}^d (see ref. [10]).

The results for the final values of the electron transfer probability over a range of initial kinetic energies are shown in fig. 5. As the energy increases, the oscillations become more rapid and their amplitudes increase. These oscillations are a general result for systems that undergo electron transfer between nearly resonant energy levels [15]. The rate of the oscillations depend on a phase which is proportional to a time integral of the difference of the ionic and neutral potentials (see Lichten [15] for details). The observation of these would provide detailed information about the interaction potentials. An average over impact points could perhaps dampen the oscillations but one should still obtain a noticeable increase in the ionization probability as the initial kinetic energy increases. It is encouraging that the rather restricted system treated here yields results for the ionization probability that have the correct order of magnitude. The sensitivity of the final probability on the initial kinetic energy suggests that momentum transfer and multiple collisions may play an important role.

4. Discussion

This paper has been primarily concerned with three major aspects of the description of gas-surface collisions that involve electron transfer by near-resonant charge-exchange processes. These are the characterization of the surface, the determination of the gas-surface interaction potentials and couplings and the description of the evolution of the nuclear and electronic variables.

The localized view of the surface, i.e. five atom cluster, allows the use of well established procedures to

determine its electronic properties. With these properties, it is relatively straightforward to construct well defined gas-surface interaction potentials and couplings. An advantage of using this procedure is that it avoids introducing expressions (coupling integral matrix, variation of energy levels) that are difficult to evaluate from first principles. Thus this approach has no adjustable parameters.

Improvements in the electronic description of the surface can be made in two areas. The first is to increase the number of surface atoms and or include a layer of atoms beneath the surface. This is well within the capability of the DIM procedure presented in ref. [9]. The second area of refinement is to employ a more realistic description of component diatomics. Inclusion of p and d orbitals or more valence electrons is within the capability of the DIM scheme but it would require further information about the diatomic eigenvalues. A major effect of making these improvements is to increase the surface's density of states. This would lead to a greater number of states that couple and it would be of interest to determine how this influences the final probabilities.

This model can be expanded in a number of ways concerning the gas surface collision dynamics. The results of the previous section show a strong dependence of the ionization probability on the initial kinetic energy of the sodium atom. It would be of interest to allow the surface atoms to move during the course of the collision so that the sodium can exchange momentum with the surface. A comparison with the results of sect. 3 would give an indication of the importance of momentum transfer in determining the ionization probability.

An important extension of this model would be to increase the number of electronic states that couple. The selection of a neutral state of A_2 or B_2 symmetry results in a three electronic state problem. This selection doubles the number of ionic states that interact with the neutral state and it would be of interest to see if this appreciable enhances the ionization probability.

The above discussion points out an important aspect of this approach from a diagnostic point of view. The approximations that are made are capable of being systematically improved or eliminated. This allows one to deal with a particular aspect of the problem (e.g. momentum transfer) and determine its relative importance in the dynamics of the collision process. Thus the accuracy of the approximations that are used can be assessed.

The theory presented here is also applicable for describing electron stimulated desorption - ESD [4] and secondary ion mass spectrometry - SIMS [16] experiments. In these cases the adsorbed particle would initially be close to the substrate interacting via one of the potential surfaces. For ESD the initial surface chosen would presumably be repulsive whereas for SIMS the initial state is attractive. The motion of the desorbing

particle need only be followed on the outward path. The ionization probabilities can then be determined as a function of exit angle and velocity.

In conclusion, an alternative procedure for describing gas-surface interactions has been presented. Although the surface is represented by a small cluster of atoms, it results in well-defined interaction potentials and couplings that contain no arbitrary parameters. The potentials and couplings can be used in formalisms that have been successful in describing gas phase reactions. We feel that this approach has the capacity of providing a detailed understanding of gas-surface reactions.

The financial support of the Office of Naval Research, IBM, and the Camille and Henry Dreyfus Foundation is gratefully acknowledged.

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