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Charge Exchange in Gas–Surface Collisions: The Three Electronic State System

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A theoretical treatment of near-resonant charge exchange occurring in gas–surface collisions is presented for a coupled three electronic state system. The surface is represented by a cluster of five metal atoms and the diatomics in molecules procedure is used to construct the gas–surface interaction potentials and nonadiabatic couplings. These are used in the common eikonal formalism which gives a time-dependent description for the evolution of the transition amplitudes and the nuclear positions and momenta. An application is made to a hyperthermal energy sodium atom scattering off a tungsten (110) surface. Results of the ionization probability vs. the initial kinetic energy of the sodium atom are presented. The three electronic channels correspond to a neutral (the initial state) and two ionic channels. In comparison to the two state results, it is found that the extra ionic channel gives rise to additional interference effects but it does not substantially increase the ionization probability.

I. Introduction

Near-resonant charge exchange between a gas atom and a solid surface is a phenomenon that occurs in many surface science experiments. The electron transfer takes place between energy levels of the gas and those of the surface that lie energetically close to each other, possibly only for a short time during the scattering process. Transitions between these levels are strongly influenced by the nuclear motions and are referred to as nonadiabatic transitions. From a theoretical point of view, at least two electronic states for the nuclear motion must be included in the description of the charge-exchange process. Ab initio solutions of the nuclear Schrodinger equation are difficult to obtain so that many approaches (as is the case here) employ semiclassical techniques to determine the final values of the transition probabilities. We have previously reported studies of a two electronic state system consisting of a neutral and an ionic channel.[1,2] The problem with relating a two electronic state calculation to gas–surface processes is that in the solid there is generally a band of states that can interact with the gas atom level and presumably this continuum of states will influence the electron-transfer rate. As an attempt to assess the importance of close-lying surface electronic levels we present here a study of charge exchange with three levels, one corresponding to a neutral atom and two to an ion. We have chosen to maintain discrete energy levels, rather than introduce continuum like features as other workers have done,[3-7] as the choice of potential surfaces and coupling matrix elements is well prescribed by the electronic structure procedure.

There have been numerous theoretical studies of gas-phase collisions that involve charge (electron) exchange where three or more electronic states are energetically accessible. Most of these studies employ semiclassical techniques based on solving the time-dependent electronic Schordinger equation with an assumed (e.g., rectilinear or Coulomb) nuclear trajectory to calculate the electron capture cross sections. Even though this present study involves charge exchange between a gas atom and a metal surface, the construction of the interaction potentials and nonadiabatic couplings and the semiclassical description of the collision dynamics are based on techniques that were developed for gas-phase systems. It therefore seems appropriate to make a few general comments on these previous studies in order to help orient this work.

The majority of the theoretical treatments of multistate electron exchange has been done in ion–atom collisions.[8] One-electron systems (e.g. bare nucleus scattering off a hydrogen atom) have been extensively investigated. This is because they are, compared to many electron systems, much simpler to solve yet they contain most of the theoretical aspects (sans electron correlation) of the more complicated systems. These theoretical aspects include the selection of the electronic basis set, the origin dependence (momentum transfer) of the electron transfer cross section, and the prescription of the nuclear trajectories.

At collision energies of kiloelectronvolts and above, there are often many (five or more) energetically open electronic channels, especially when a large nuclear charge asymmetry is present. These channels become populated by both angular (Coriolis) couplings at usually small internuclear separations and radial couplings (often of the Landau–Zener type) at larger internuclear separations. The convergence of the cross sections with respect to both the type and size of the electronic basis has been a major subject of theoretical interest. Generally, molecular orbitals provide a good description at small internuclear distances whereas atomic orbitals are more appropriate at large distances. There have been numerous calculations that employ molecular orbitals[9] (perturbed stationary state) or atomic orbitals (possibly appended with united atom orbitals)[10] and recently a procedure that

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(1) Olson, J. A.; Garrison, B. J. *J. Chem. Phys.* **1985**, *83*, 1392.
(2) Olson, J. A.; Garrison, B. J. *Nucl. Instrum. Methods*, in press.
(3) Blandin, A.; Nourtier, A.; Hone, D. W. *J. Phys. (Paris)* **1976**, *37*, 369.
(4) Norskov, J. K.; Lundqvist, B. I. *Phys. Rev. B* **1979**, *19*, 5661.
(5) Brako, R.; Newns, D. M. *Surf. Sci.* **1981**, *108*, 253.
(6) Lang, N. D. *Phys. Rev. B* **1983**, *27*, 2019.
(7) Tully, J. C. *Phys. Rev. B* **1977**, *16*, 4324.
(8) McDowell, M. R. C.; Coleman, J. P. *Introduction to the Theory of Ion-Atom Collisions*; North-Holland: Amsterdam, 1970.
(9) Wada, K.; Murai, T. *J. Phys. B* **1985**, *18*, 4259.

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transforms from molecular to atomic orbitals has been proposed.[11,12] One would expect however that, as the collision energy decreases, the molecular orbital description would provide a better electronic representation.

The problem of the origin dependence of the electron-transfer cross section has been known for some time.[13] For simplicity, consider a single electron that is transferred from nucleus A to nucleus B. Before the collision, the electron has a velocity due to its orbital motion and an additional velocity resulting from its association with nucleus A. If the electronic origin is chosen to be A, this latter velocity is zero whereas if the origin is B, it is the relative collision velocity. For an origin somewhere on a line joining A and B, this velocity is between these limits. After the collision, the same situation exists due to the electron's association with B. Therefore there is in general a change in the velocity of the electron during the collision which is not accounted for in the Born–Oppenheimer solutions of the electronic Hamiltonian. As the collision velocity increases, this velocity change or momentum transfer becomes more important. This origin dependence can be removed by including electron translation factors[14] and several schemes are available for constructing them (see ref 15 and papers cited therein).

The last theoretical aspect of interest here involves the choice of the nuclear trajectory. Most of the semiclassical studies use impact parameter methods that employ either rectilinear or Coulomb trajectories. At collision energies of kiloelectronvolts and above, the use of rectilinear trajectories in small angle scattering introduces little error.[16] However at lower collision energies, a noticeable dependence of the cross section on the nuclear trajectory has been reported.[17] This suggests that extra care is needed in defining the nuclear trajectory at these lower collision energies.

This study involves hyperthermal energy (5–50 eV) collisions of a sodium atom with a tungsten surface. At these energies, a molecular orbital representation is appropriate and is obtained from the diatomics in molecules[18,19] procedure. This procedure has the advantage of ensuring the proper description of the asymptotic channels. The tungsten surface consists of a five-atom cluster of which four of the atoms lie at the corners of a parallelogram with dimensions corresponding to the (110) crystal face. The fifth atom lies at the center of the other four atoms and the sodium atom approaches perpendicular to it. The details of the procedure used to construct the gas–surface interaction potentials and nonadiabatic couplings have been presented elsewhere[1] and only the results are used here. At hyperthermal energies the momentum transfer of the electron is so small that it can be neglected so that electron translation factors are not included.

The mean trajectory procedure based on using a common eikonal[20] is used to solve for the collision dynamics. This procedure results in a coupled set of time-dependent Hamilton-like equations that self-consistently determine the transition amplitudes and the nuclear positions and momenta. The self-consistency results from the requirement that the trajectories for the nuclear positions and momenta satisfy the conservation of energy principle. Thus much of the arbitrariness of the trajectories used in other treatments is avoided. The use of a mean trajectory is an approximation and recently a comparison between quantal and common eikonal transition probabilities for the two state case were reported.[21] At low energies (below 25 eV) the results essentially agree. At higher energies the overall trends of the quantal results were followed but the Stuckelberg oscillations were not quantitatively reproduced.

The initial studies[1,2] were done for a coupled two electronic state system consisting of a neutral channel (the initial state) and an ionic channel. Final values of the electron-transfer probabilities were calculated as a function of the initial kinetic energy of the sodium atom which varied between 5 and 50 eV. The results showed an overall increase of the electron-transfer probability as the kinetic energy of the sodium atom increased. The disagreement with the experimental observations[22] of almost unit probability for electron transfer was most noticeable at the lowest energies. There were also rapid oscillations in the calculated ionization probabilities which are due to an interference between the neutral and ionic pathways.[23]

In the work presented here, an additional ionic channel is included in the calculation. To our knowledge, this is the first treatment of electron transfer at metal surfaces that employs a discrete electronic representation consisting of three electronic channels. The primary objective is to determine how this extra ionic channel influences the electron-transfer probability. This should also give some insight into how electron transfer at metal surfaces is affected by a continuum of surface electronic states. In section II, a brief presentation of the formalism needed in the three-state calculations is presented. Results for the ionization probability for the three-state system are presented and compared to the separate two-state systems in section III. The paper closes with conclusions in section IV.

II. The Three Electronic State System

There are three major problems that must be solved in our treatment of electron transfer at metal surfaces. The first problem involves finding the solutions for the eigenvalues and eigenfunctions of the neutral and ionic surfaces. A five-atom cluster is used to represent the surface and its electronic properties are solved for within the diatomics in molecules procedure.[19] The second problem entails the construction of the gas–surface interaction potentials and nonadiabatic couplings. The surface eigenfunctions are used to construct an electronic basis and the potentials and nonadiabatic couplings are again obtained within the diatomics in molecules framework. The details of this procedure are given in ref 19 and 1. These adiabatic potentials and nonadiabatic couplings are transformed into diabatic potentials which are used in the common eikonal formalism to solve for the transition amplitudes. The common eikonal formalism has been treated in detail elsewhere[1,20,24] and only a brief sketch of it is presented here. Throughout this treatment, the positions of the surface nuclei are held fixed and the perpendicular approach of the sodium atom to the center tungsten atom is used. Also given here is a brief overview of the procedure used to obtain the unitary transformation needed in going from the adiabatic to diabatic electronic representation for the three-state system.

For the one-dimensional system considered here, the solutions of the time-independent nuclear Schrodinger equation satisfy

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dR^2} + V^d\right)\psi(R) = E\,\psi(R) \qquad (1)$$

where R is the separation of the sodium atom from the surface and m is the mass of the sodium atom. For a three electronic state system, V^d is the (3×3) matrix representation of the electronic Hamiltonian in the diabatic representation and ψ is the (3×1) column vector of the nuclear amplitudes. The solutions of eq 1 are written in the form

$$\psi(R) = \chi(R)e^{(i/\hbar)S(R)} \qquad (2)$$

where $S(R)$ is the common (for all electronic channels) eikonal. Substituting eq 2 into eq 1, invoking the short wavelength approximation, and transforming into time results in a set of coupled

(10) Fritsch, W.; Lin, C. D. *Phys. Rev. A* **1984**, *29*, 3039.
(11) Kimura, M.; Lin, C. D. *Phys. Rev. A* **1985**, *31*, 590.
(12) Kimura, M.; Lin, C. D. *Phys. Rev. A* **1985**, *32*, 1357.
(13) Bates, D. R.; Massey, H. S. W.; Stewart, A. L. *Proc. R. Soc. London, Ser. A* **1953**, *216*, 437.
(14) Bates, D. R.; McCarroll, R. *Proc. R. Soc. London, Ser. A* **1958**, *245*, 175.
(15) Riera, A. *Phys. Rev. A* **1984**, *30*, 2304.
(16) Bates, D. R.; Boyd, A. H. *Proc. Phys. Soc.* **1962**, *79*, 710.
(17) van Hemert, M. C.; van Dishoeck, E. F.; van der Hart, J. A.; Koike, F. *Phys. Rev. A* **1985**, *31*, 2227.
(18) Ellison, F. O. *J. Am. Chem. Soc.* **1963**, *85*, 3540.
(19) Olson, J. A.; Garrison, B. J. *J. Chem. Phys.* **1984**, *81*, 1355.
(20) Micha, D. A. *J. Chem. Phys.* **1983**, *78*, 7138.
(21) Currier, R.; Herman, M. F. *J. Chem. Phys.* **1985**, *82*, 4509.
(22) Overbosch, E. G.; Rasser, R.; Tanner, A. D.; Los, J. *Surf. Sci.* **1980**, *92*, 310.
(23) Lichten, W. *Phys. Rev. A* **1965**, *139*, A27.
(24) Olson, J. A.; Micha, D. A. *J. Chem. Phys.* **1984**, *80*, 2602.

first-order equations of the form

$$\frac{\hbar}{i}\frac{d}{dt}C_i(t) = V^d_{ii}C_i(t) + \sum_{i\neq j} V^d_{ij}C_j(t) \quad (3)$$

where the C_i's are just, within a phase factor, the time-dependent $\chi_i(R(t))$. Equations 3 can be recast into the form of Hamilton's equations of motion by defining the Hamiltonian as

$$H(R,P,C) = \frac{P^2}{2m} + \bar{V} \quad (4)$$

where for three electronic states ($C_j = (C^r_j + iC^i_j)/(2\hbar)^{1/2}$

$$\bar{V} = \sum_{j=1}^{3} V^d_{jj}(C^{r2}_j + C^{i2}_j) + 2\sum_{k>j} V^d_{kj}(C^r_k C^r_j + C^i_k C^i_j) \quad (5)$$

and the momentum, P, is defined as

$$P(t) = \frac{dS(R(t))}{dt} \quad (6)$$

With eq 5, eq 4 can be reexpressed as

$$\frac{dC^r_j}{dt} = -\frac{\partial H}{\partial C^i_j} = -2\sum_{k=1}^{3} V^d_{jk}C^i_k \quad (7)$$

$$\frac{dC^i_j}{dt} = \frac{\partial H}{\partial C^r_j} = 2\sum_{k=1}^{3} V^d_{jk}C^r_k \quad (8)$$

which have the form of Hamilton's equations of motion. In eq 7 and 8, the real and imaginary parts of the transition amplitudes form sets of canonical variables. A convenient choice for the trajectories of $R(t)$ and $P(t)$ is furnished by requiring that there be conservation of energy thus

$$\frac{dR}{dt} = \frac{\partial H}{\partial P} = \frac{P}{m} \quad (9)$$

$$\frac{dP}{dt} = -\frac{\partial H}{\partial R} = -\frac{\partial \bar{V}}{\partial R} \quad (10)$$

Equations 7–10 are a coupled set of differential equations that self-consistently determine the nuclear transition amplitudes. The probability, P_i, of emerging in the electronic channel "i" after the collision is over is

$$P_i(\infty) = C^*_i(\infty)C_i(\infty) \quad (11)$$

As is seen in eq 5, the potential in the Hamiltonian is an average potential so that the nuclear position and momentum cannot be strictly interpreted as the classical position and momentum.

The electronic Hamiltonian in eq 1 is defined in the diabatic electronic representation. Since potential energy surfaces are generally obtained in the adiabatic representation, a unitary transformation relating the two schemes needs to be constructed. The diabatic representation proposed by Smith[25] which rigorously gives the null matrix for the electronic representation of the nuclear momentum operator is used here. In this procedure the unitary transformation satisfies a first-order differential equation in the variable R of the form

$$\frac{dA(R,R_0)}{dR} + \mathbf{d}^a A(R,R_0) = 0 \quad (12)$$

where $R_0 = \infty$ and the boundary condition is that $A(R_0,R_0) = 1$. For three electronic states, eq 12 is a (3 × 3) matrix equation and the coupling matrix, $\mathbf{d}^a$, has the form

$$\mathbf{d}^a = \begin{bmatrix} 0 & d^a_{12} & d^a_{13} \\ -d^a_{12} & 0 & d^a_{23} \\ -d^a_{13} & -d^a_{23} & 0 \end{bmatrix} \quad (13)$$

where

$$d^a_{ij} = |\langle \Psi^a_i | \frac{d}{dR} | \Psi^a_j \rangle| \quad (14)$$

(25) Smith, F. T. *Phys. Rev.* **1969**, *179*, 111.

i.e., the coupling between the adiabatic states i and j and $\langle ...|... \rangle$ indicates an integration over electronic coordinates only. A general procedure for constructing the transformation for the three-state case has been given by Top and Baer[26] and only the results of this procedure are presented here. In general it is possible to express the transformation as a product of three matrices, $Q_1(\gamma)$, $Q_2(\phi)$, and $Q_3(\theta)$ where

$$[Q_l(\alpha)]_{ij} = \bar{\delta}_{il}\bar{\delta}_{jl}(1 - 2\Xi_{ij})(\delta_{ij}\cos\alpha + \bar{\delta}_{ij}\sin\alpha) + \delta_{il}\delta_{jl} \quad (15)$$

where δ_{ij} is the Kronecker delta function

$$\bar{\delta}_{ij} = 1 - \delta_{ij} \quad (16)$$

$$\Xi_{ij} = 1 \text{ for } i > j \quad (17)$$

$$= 0 \text{ for } i \leq j$$

and α is γ, ϕ, and θ for Q_1, Q_2, and Q_3, respectively. The matrix elements of the transformation are obtained from

$$A_{mn} = \sum_i \sum_j [Q_1(\gamma)]_{mi}[Q_2(\phi)]_{ij}[Q_3(\theta)]_{jn} \quad (18)$$

From eq 12 it is not difficult to show that the angles satisfy

$$\frac{d\phi}{dR} = -(d^a_{12}\sin\gamma + d^a_{13}\cos\gamma) \quad (19)$$

$$\frac{d\gamma}{dR} = (d^a_{12}\cos\gamma - d^a_{13}\sin\gamma)\tan\phi - d^a_{23} \quad (20)$$

$$\frac{d\theta}{dR} = -(d^a_{12}\cos\gamma - d^a_{13}\sin\gamma)(\cos\phi)^{-1} \quad (21)$$

The boundary conditions chosen for $R_0 = \infty$ are that $\theta = \phi = \gamma = 0$. These equations are numerically integrated over R throughout the collision. The diabatic matrix elements of the electronic Hamiltonian are

$$V^d_{ij} = \sum_k V^a_k A_{ki} A_{kj} \quad (22)$$

where the A_{ij} are defined in eq 18 and the V^a_k are the adiabatic eigenvalues.

The general prescription for performing the calculation begins with the selection of the initial conditions for eq 7–10. In all cases the initial electronic state corresponds to the neutral channel (channel 3) so that, initially, $P_3 = 1$ and $P_1 = P_2 = 0$. The initial separation from the surface (R) is chosen sufficiently large (10 Å) so that the Na–W(110) interaction is negligible. Prescribing the initial kinetic energy, E^i_k, determines the initial momentum

$$P(t=0) = -(2mE^i_k)^{1/2} \quad (23)$$

The calculations are simplified somewhat by modeling the nonadiabatic couplings with a Gaussian so that

$$d^a_{ij} = a_{ij}e^{-b_{ij}(R-R_{ij})^2} \quad (24)$$

where a_{ij} is the maximum value of the coupling and R_{ij} is the distance where the maximum occurs. The parameter b_{ij} is chosen such that the integral over R of eq 14 and the absolute value of eq 24 are equal.

The calculation consists of numerically integrating[27] in time eq 7–10. At each integration point the adiabatic potentials and couplings are calculated. Equations 19–21 are numerically integrated to the corresponding distance which gives the transformation angles at the point R. These angles define the transformation matrix which furnish the diabatic potentials at the distance R. Equations 7 through 10 are evaluated, the time is incremented, and the procedure is repeated. This is continued until well after the collision is over which furnishes from eq 11 the final values of P_1, P_2, and P_3. Another probability of interest is the total ion fraction P^{ion}. It is defined as

$$P^{ion} = P_1(\infty) + P_2(\infty) \quad (25)$$

(26) Top, Z. H.; Baer, M. *J. Chem. Phys.* **1977**, *66*, 1363.
(27) Shampine, L. F.; Gordon, M. K. *Computer Solutions of Ordinary Differential Equations: The Initial Value Problem*; Freeman: San Francisco, 1975.

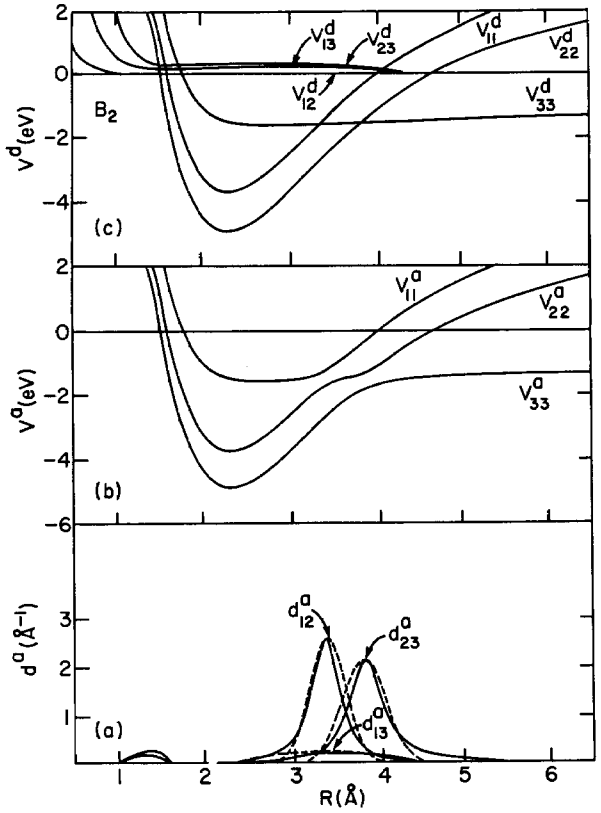

Figure 1. Potentials and nonadiabatic couplings for the states of B_2 symmetry. (a) Nonadiabatic couplings: (—) calculated couplings, (---) modeled couplings. (b) Adiabatic potentials. (c) Diabatic potentials.

TABLE I: Coefficients of the Gaussians Used To Model the Nonadiabatic Couplings

ij	a_{ij}	b_{ij}	R_{ij}
12	2.60	11.6	3.44
13	0.25	1.45	3.38
23	2.18	8.09	3.86

which is the sum of the transition probabilities for emerging in the two ionic channels. This is also referred to as the total electron-transfer probability.

III. Results

In this section results for the transition probabilities as a function of the initial kinetic energy of the sodium atom for a three electronic state system are presented. The three electronic states that effectively couple are those of B_2 symmetry from our previous study of the interaction potentials of a Na atom interacting with the five-atom W substrate. The system consists of one asymptotically neutral state and two asymptotically ionic states. The neutral state always corresponds to the initial electronic channel.

The adiabatic gas–surface interaction potentials and nonadiabatic couplings for the B_2 symmetry states are shown in Figure 1, b and a, respectively. This system exhibits two avoided crossings in the regions where the nonadiabatic couplings are the largest. The parameters used to model the couplings are given in Table I and the modeled couplings are also shown in Figure 1a. Carrying through the procedure of the preceding section results in the diabatic potentials displayed in Figure 1c. The avoided crossings present in the adiabatic case are replaced by actual crossings in the diabatic case. The nonadiabatic couplings are replaced by the off-diagonal matrix elements of the electronic Hamiltonian in the diabatic representation. The divergence of these off-diagonal terms at small distances is a consequence of θ, ϕ, and γ not being equal to $\pi/2$ in this region.

Results for a typical trajectory with an initial kinetic energy of 50 eV are shown in Figure 2. The plot of R vs. t (Figure 2a) shows that the sodium atom approaches the surface, undergoes

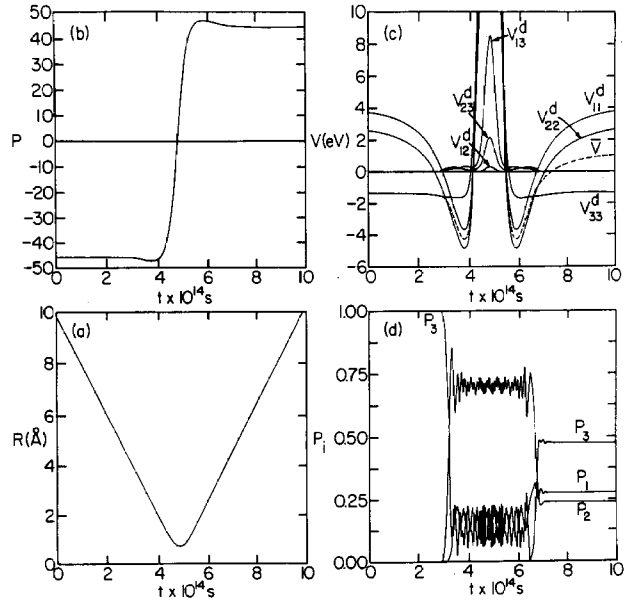

Figure 2. Trajectory results for an initial kinetic of 50 eV. (a) R vs. t. (b) P vs. t. The unit of P is 3.8×10^{-17} g cm/s. (c) V (dashed line) and the diabatic potentials vs. t. (d) P_1, P_2, and P_3 vs. t.

a single collision, and departs. The momentum, P, is initially negative and constant as the sodium atom approaches the surface (Figure 2b). Near the surface the magnitude of P increases due to the influence of the ionic well. At the turning point P is zero and it becomes positive and constant after the collision is over. Initially $\bar{V}$ (dashed line in Figure 2c) coincides with V_{33}^d the neutral potential. Near the surface it resembles the ionic potential, V_{22}^d, which indicates that the electron is transferred to the surface during the initial part of the collision. After the collision $\bar{V}$ lies between the ionic and neutral potentials which emphasizes its average nature. There are two regions where the probabilities (Figure 2d) undergo large changes which correspond to the regions where the diabatic potentials cross. The rapid oscillations between these regions are due to the divergence of the off-diagonal potential terms.

The results for the final values of the transition probabilities, P_2 and P_1, and the total ion fraction, P^{ion}, as a function of the initial kinetic energy are shown in Figure 3, a, b, and c, respectively. There are two main features worth noting in these results. The first is that over the entire range of kinetic energy the contribution of P_1 to P^{ion} is on the average substantially less than that of P_2. The second is that there seems to be rapid oscillations in the P^{ion} and P_2 vs. E_k^i curves that are superimposed on much more gradual ones.

There are two possibilities that could lead to the relatively small contribution of P_1 to P^{ion}. These possibilities are that either channels 1 and 3 do not couple effectively or that the neutral flux that survives the initial crossing between channels 2 and 3 is relatively small. In order to test the first possibility, separate two-state calculations were done for the systems (V_{22}^d, V_{33}^d) and (V_{11}^d, V_{33}^d). The results for the ionization probability for the systems (V_{22}^d, V_{33}^d) and (V_{11}^d, V_{33}^d) vs. the initial kinetic energy are shown in Figure 4, a and b, respectively. A comparison of parts a and b of Figure 4 clearly demonstrates that both separate two-state systems lead to roughly the same ionization probability. Therefore the relatively small contribution of P_1 to P^{ion} must be due to a rather large loss of neutral flux at the initial crossing (V_{22}^d, V_{33}^d). This in part is a consequence of the hyperthermal energies used here. At these energies, the system tends to evolve on the lowest adiabatic potential (V_{33}^a) which corresponds to a diabatic transition from channel 3 to channel 2 during the initial part of the collision. Since the coupling between the ionic channels is small (d_{13}^a in Figure 1a), the ionic flux remains in channel 2 until the potentials V_{22}^d and V_{33}^d cross on the outward path. Thus on both the inward and outward paths, the crossing between V_{22}^d and V_{33}^d accounts for most of the change in probability. This picture becomes less

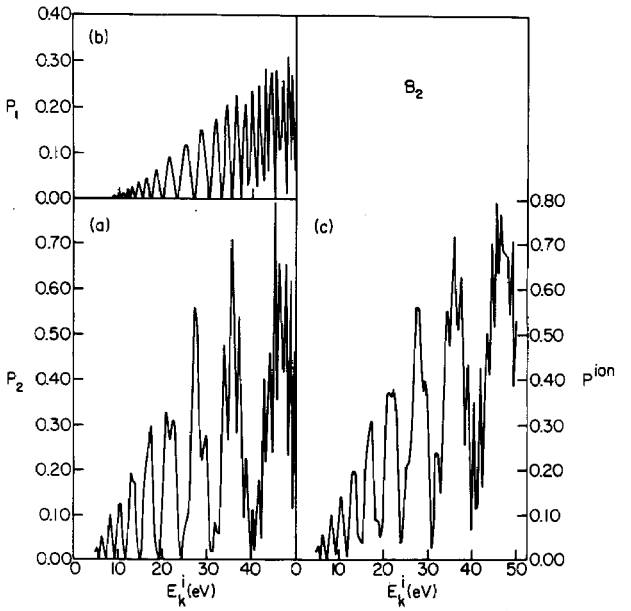

Figure 3. Final values of the probabilities as a function of the initial kinetic energy. (a) P_2 vs. E_k^i. (b) P_1 vs. E_k^i. (c) P^{ion} vs. E_k^i.

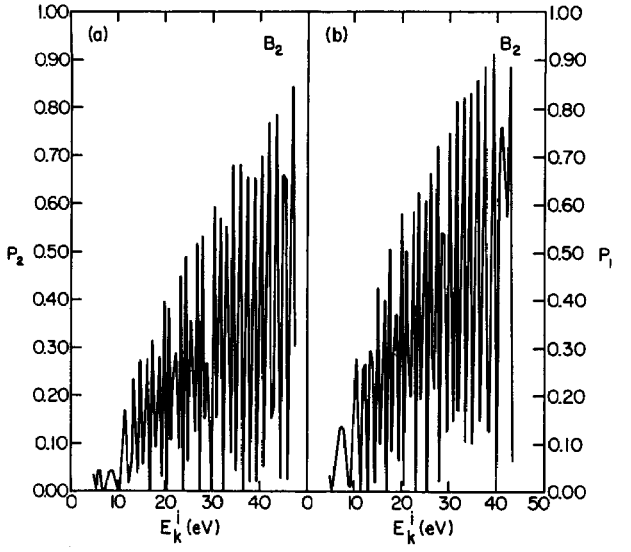

Figure 4. Final values of the electron-transfer probability vs. E_k^i for the separate two-state systems. (a) The two states correspond to the V_{22}^d and V_{33}^d potentials. (b) The two states correspond to the V_{11}^d and V_{33}^d potentials.

valid at higher collision energies.

The oscillatory behavior of the electron-transfer probability has been theoretically interpreted by Lichten.[23] Generally, oscillations occur when more than one pathway leads from an initial to a final state. For a two-state system, there are two pathways corresponding to evolution on the neutral and ionic potentials that lead to each final state. For the case of a neutral initial state and an ionic final state, the first pathway corresponds to a transition to the ionic state as the Na atom approaches the surface with the Na atom remaining in the ionic state as it departs the surface. Path 2 has the Na atom remaining in the neutral state until it scatters from the surface at which point there is a transition to the ionic state. A phase difference develops between these pathways which results in an interference effect at the final crossing on the outward path. The phase difference is given by (for the V_{22}^d, V_{33}^d system)

$$\Omega = \frac{1}{\hbar}\int_0^t (V_{22}^d - V_{33}^d)\, dt \qquad (26)$$

which results in an oscillatory dependence of the electron-transfer probability given by $\sin^2(\Omega/2)$. Since the neutral and ionic potentials are relatively far apart inside the crossing, the phase difference is large resulting in the rapid oscillations seen in Figure 4.

The interpretation of the oscillations for the three-state case are a little more involved. In the following, the positions of the inner and outer crossings are designated by R_i and R_o, respectively. There are a total of eight different pathways leading from the initial neutral channel to all final channels. Of these only three lead to a final state in channel 2. Paths 1 and 2 correspond to the pathways of the V_{22}^d, V_{33}^d two-state system described above and give rise to the rapid oscillations of P_2 in Figure 3a. For path 3 the Na atom starts in the neutral channel (state 3) until the inner crossing where there is a transition to state 1. On the outward path the Na atom first makes a transition to state 3 and then to state 2. The slower oscillations arise from the interference between paths 1 and 3. A reasonable estimate of the phase difference between these paths can be obtained from an approximate form of eq 26. Transforming eq 26 to an integral over R and assuming both a constant velocity and sudden transitions leads to a phase difference between path 1 and 3 of

$$\Omega = \frac{2}{\hbar v}\left[\int_{R_i}^{R_o}(V_{33}^d - V_{22}^d)\, dR + \int_{R_{tp}}^{R_i}(V_{11}^d - V_{22}^d)\, dR\right] \qquad (27)$$

where v is the initial velocity of the sodium atom and R_{tp} is the turning point. Between R_i and R_o, V_{33}^d is nearly constant and V_{22}^d is almost linear (see Figure 1c) so that the first integral in eq 27 is approximately

$$\int_{R_i}^{R_o}(V_{33}^d - V_{22}^d)\, dR \approx \frac{\Delta E}{\Delta R}\int_{R_i}^{R_o}(R - R_o)\, dR = \Delta E(R_o - R_i)/2 \qquad (28)$$

where $\Delta E = V_{33}^d(R_i) - V_{22}^d(R_i)$ and $\Delta R = R_o - R_i$. A reasonable approximation for the second integral in eq 27 is obtained by noticing that V_{11}^d and V_{22}^d are topologically very similar. In fact, if V_{11}^d is displaced downward until its well coincides with V_{22}^d, the two curves are nearly superimposable. Therefore since $V_{33}^d(R_i) = V_{11}^d(R_i)$, the second integral becomes

$$\int_{R_{tp}}^{R_i}(V_{11}^d - V_{22}^d)\, dR \approx \Delta E(R_i - R_{tp}) \qquad (29)$$

Using eq 28 and 29 in eq 27 leads to

$$\Omega = \frac{\Delta E}{\hbar v}(R_o + R_i - 2R_{tp}) \qquad (30)$$

In the case discussed here, R_o and R_i are 3.86 and 3.44 Å, respectively, and ΔE is 1.14 eV. For a typical turning point of 1 Å, eq 30 becomes

$$\Omega = 325/E_k^{i\,1/2} \qquad (31)$$

where the kinetic energy has units of electronvolts. A calculation of $\sin^2(\Omega/2)$ between an initial kinetic energy of 20 and 35 eV leads to three maxima which is in rough agreement with the calculated results of Figure 3a. One would not expect perfect agreement since the constant velocity assumption is least valid at these low energies. However, this rather crude analysis clearly demonstrates that the slower oscillations are a consequence of the smaller phase difference between path 1 and path 3 as compared to the phase difference between path 1 and path 2.

IV. Conclusions

There are two primary conclusions that can be made from the results of this study. The first is that, at the collision energies used here, the addition of an extra ionic channel does little to enhance the total electron-transfer probability. The second conclusion is that the extra ionic channel does give rise to additional interference effects which result in much slower oscillations in P^{ion}.

The lack of enhancement of P^{ion} with the extra ionic channel is primarily a consequence of the hyperthermal energies used in this study. At these energies, the incoming sodium atom tends to remain on the lowest adiabatic potential which corresponds to

the lowest ionic diabatic potential near the surface. Therefore, most of the neutral flux is lost at the initial (outer) crossing of the neutral and lowest ionic diabatic potentials. Since the ionic states do not significantly couple, this ionic flux remains in the lowest ionic channel until it crosses the neutral potential on the outward path. As a consequence, most of the change in probability on the outward path will again be in P_2 and P_3 at the outer crossing. When the collision energy increases, this description becomes less accurate. The neutral flux which survives the initial crossing generally increases as the collision energy increases. As this neutral flux increases, including the extra ionic channel should become more important in determining the final values of the total electron-transfer probability. However, for the energy range used here, the extra ionic channel does little to increase P^{ion}. This suggests that including a third ionic channel would have practically no affect on P^{ion} at these energies.

The most noticeable effect of the extra ionic channel is that it gives rise to much slower oscillations in P_2 and P^{ion}. An analysis of these oscillations clearly shows that they can be attributed to the topological similarity of the two ionic channels. Since there is a continuous set of energy levels for a metallic surface, it is doubtful whether these slower oscillations are physically real. Of interest would be to move the ionic potentials closer to each other. This would give a better description of the continuum of surface states and provide information about how close the ionic potentials have to be in order for the extra ionic channel to play a significant role. The rapid oscillations present in the two-state results are simply a consequence of having a neutral and ionic pathway and could therefore be physically significant. Moving the ionic potentials closer to each other could give some insight into this possibility too.

Including the extra ionic channel does not improve the disagreement between theory and experiment at the lowest energies. We feel that this is most likely due to confining the transferred electron to the metal cluster. In reality, the transferred electron can travel many lattice spacings away from the collision zone during the course of the collision. This suggests that the ionic potentials of the initial and final stages of the reaction may not be the same. It would be of interest to define a realistic prescription based on the duration of the collision that would allow these ionic potentials to change during the collision. This will be the subject of future work.

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