PHYSICAL REVIEW B VOLUME 34, NUMBER 1 1 JULY 1986

Theory of charge exchange in the scattering of molecular ions from simple metals

U. Imke, K. J. Snowdon, and W. Heiland
Fachbereich Physik, Universität Osnabrück, 4500 Osnabrück, Federal Republic of Germany

(Received 24 December 1985)

A description of the charge exchange between energetic diatomic molecular ions and metal surfaces is presented, which includes in a semiclassical way the coupling between the available exit channels. Explicit results for resonant electron capture during the scattering of H_2^+ from Al(110) are given. For low incident energies, capture to both the $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states occurs on the incident portion of the trajectory. Capture to the singlet state predominates for molecule-axis orientations nearly parallel to the surface, and to the triplet state for near-normal orientations. The axis-orientation dependence of the triplet occupation probability and the dissociation-fragment relative kinetic-energy distribution are calculated, as is the vibrational population distribution of the singlet ground state.

I. INTRODUCTION

A fundamental understanding of energetic molecule-surface interactions is becoming increasingly relevant in fields as diverse as astrophysics, fusion research, and the solid catalyst and microelectronic industries. To cite just one example, the recent development of high-power hydrogen neutral beams for auxiliary heating in tokamak plasma devices that either use the molecular ion-surface charge exchange as a primary step in H^- beam formation, or the efficiency of positive ion production in the source is determined in part by molecular-ion—surface interactions.[1-3] Only a detailed understanding of the energy and charge exchange on the atomic level will ensure the optimum performance of practical devices.

Our theoretical understanding of the energetic atomic-ion—surface interaction has shown considerable progress in recent years.[4-15] Motivated by the observation of neutralization, dissociation, and rotational, vibrational, and electronic excitation of scattered, sputtered, and desorbed molecules,[16-22] attempts have been made to formulate a corresponding theory of energetic molecule-surface interactions. Excitation of the "mechanical" modes (vibration and rotation) has been modeled by Parilis,[23,24] Snowdon *et al.*,[25] Sigmund *et al.*,[26] and Avouris *et al.*,[27] with quite good agreement between model predictions and experiment.

Early studies of molecular dissociation following molecular-ion—surface scattering[16,17] led to the proposal, further expanded in Ref. 18 that charge capture to antibonding states is an important dissociation channel. The quantitative description of this dissociation mechanism was outlined briefly for the first time in Ref. 21, and used to derive, from experimental measurements, the dependence of the charge exchange probability on level-energy position within the substrate density of states. This is unique information not obtainable from measurements using atomic-ion projectiles, and provides one motivation for the extra theoretical and experimental effort required.

This paper presents the first parameter-free quantitative description of the time-dependent energetic molecular-ion—metal-surface charge exchange problem, emphasizing the electronic coupling. Semiempirical models for the total cross sections, in which the neutralization probability is treated as a fitting parameter, already exist,[28,29] as do models for energy loss mediated by charge transfer in the harpooning mechanism.[30] Our approach is analogous to that currently used to model the atomic-ion—metal surface interaction.[14,15] The resonant coupling matrix elements, including their molecular-axis-orientation dependence, are explicitly calculated in the accompanying paper[31] (hereafter referred to as II), and used here to determine the probability for resonant charge capture to the lowest-lying singlet and triplet states of H_2 following scattering from an aluminum surface.

II. THEORY

A. Definition of the problem

The scattering of an energetic molecular ion from a metal surface may be accompanied not only by a change in direction, but by energy loss by the center of mass, rotational and vibrational excitation, charge exchange, and electronic excitation of both the molecule and substrate. This is clearly a complex many-body problem, which we do not attempt to solve here. Rather, we will assume experimental conditions have been chosen such that negligible rotational and vibrational excitation (via direct momentum transfer) and substrate electronic excitation occurs. For sufficiently low velocities, the total Hamiltonian may be separated into electronic and nuclear parts, viz.,

$$H = H_e + H_n \ , \tag{1}$$

where H_e is dependent also on the nuclear coordinates. Transitions into and out of a particular electronic state depend then on the energetic position of that state compared to empty and filled states in the substrate. As for atoms, both resonant and Auger transitions are posssible (Fig. 1). In all cases, since electronic transitions are fast compared to molecular vibration times, the initial internuclear coordinate or R_i distribution before the scattering interaction confines electronic transitions to other poten-

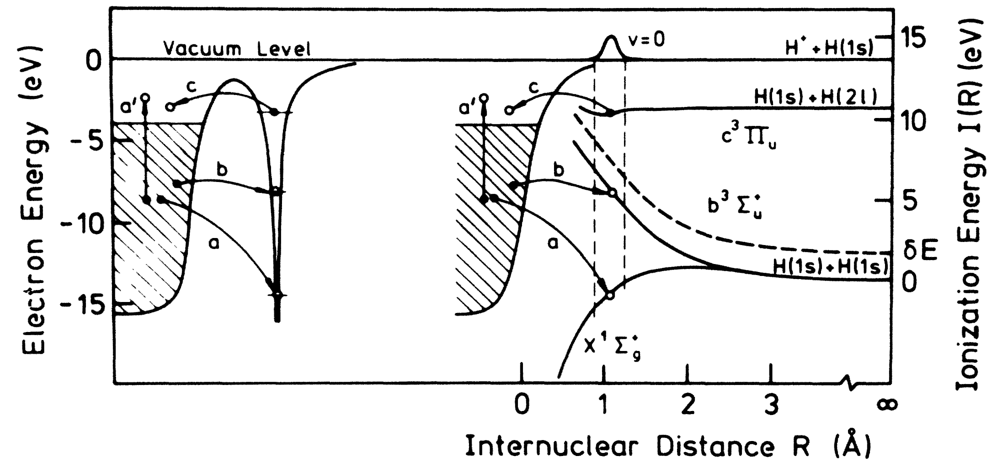

FIG. 1. Schematic illustrations of charge exchange between atoms (left) and molecules (right) and metals. The metal density of states corresponds to that of Al(110). Auger capture to the ion is represented by *aa'*, resonant capture by *b*, and resonant ionization of a neutral atom or molecule by *c*. Both capture mechanisms are energetically allowed for all states below the Fermi level. Both diagrams correspond to a particular distance of the atom or molecule from the surface, the internuclear distance coordinate *R* being that between the two hydrogen atoms of the molecule. The Franck-Condon principle restricts transitions to the *R* range defined by the initial state. For $H_2^+(v=0)$ as initial state, this corresponds to the region between the dashed vertical lines. To first order, the image-potential-induced shift δE of the molecular level changes only the relative position of the curve $I(R)$ with respect to the metal-electron density of states (dashed curve).

tial surfaces to this R_i range. This is just the Franck-Condon principle, and is illustrated in Fig. 1 for the neutralization of a ground vibrational state H_2^+ ion into the lowest-lying singlet and triplet states of the H_2 molecule.

The possible consequences of this charge exchange are twofold and can be seen by reference to Fig. 2. If a transition occurs to a bound state, with an equilibrium internuclear separation different from that in the initial ionized state, vibrational excitation is expected. If the transition occurs to an unbound portion of a molecular potential surface, the molecule will dissociate. The initial R_i distribution directly defines the relative kinetic-energy distribution of the fragments. These arguments apply equally to polyatomic molecules.

As a consequence of (1) the probability for a transition from a molecular ionic state A^+ in vibrational state v_i with instantaneous internuclear separation R_i to the neutral state A^0 in vibrational state v_f can be written as

$$Q_{v_f A^0}=P_{A^0}\,|\langle \psi_{v_i A^+}|\psi_{v_f A^0}\rangle|^2 , \tag{2}$$

where P_{A^0} represents the occupation probability following the interaction, and $\psi_{v_i A^+}$ and $\psi_{v_f A^0}$ are the initial- and final-vibrational-state wave functions.

For transitions to bound molecular states, this equation can be used to determine the final-vibrational-state population distribution of A^0. For a transition to an unbound state, $\psi_{v_f A^0}$ is a continuum wave function and can be approximated well by

$$\psi_{v_f A^0}=k\delta(R-R_i) , \tag{3}$$

where k is a normalization factor;[33] Eq. (2) then reduces to

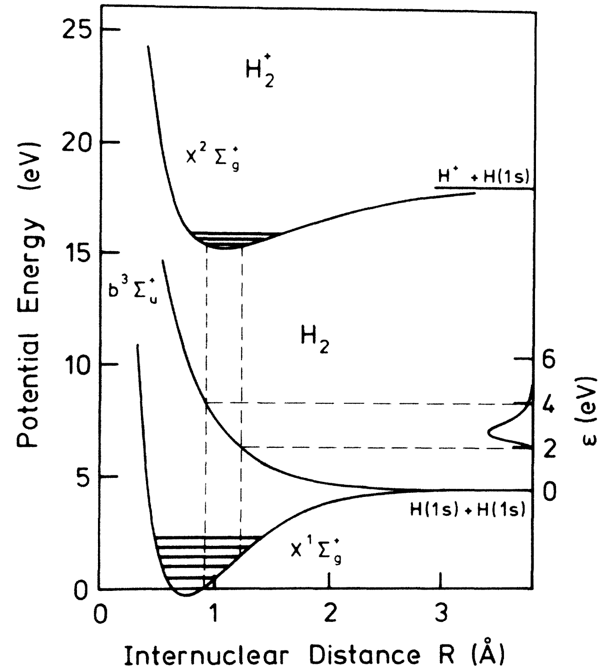

FIG. 2. Potential curves of H_2 and H_2^+ (Ref. 32) corresponding to the energetically allowed H_2^+ neutralization reactions during scattering from an Al(110) surface (Fig. 1). For $v=0$ only populated in the incident beam, the Franck-Condon principle qualitatively predicts vibrational excitation of the H_2 $X\,^1\Sigma_g^+$ product, namely, to $v=1$, 2, and 3, and a dissociation-product relative kinetic-energy distribution peaking between 2 and 4 eV (shown schematically on the right).

$$Q_{v_f A^0}=P_{A^0}\,|\,\psi_{v_i A^+}(R_i)\,|^2 \,. \tag{4}$$

A dissociative-charge-exchange experiment measures the distribution of fragments of relative-kinetic-energy ε. The coordinate transformation $R_i \rightarrow \varepsilon$ performed on the above expression leads to the energy spectrum

$$\frac{dN}{d\varepsilon}=\frac{dR}{d\varepsilon}\bigg|_{R_i} P_{A^0}\sum_{v_i} c_{v_i}\,|\,\psi_{v_i A^+}(R_i)\,|^2 \,, \tag{5}$$

where we have assumed the energy width of P_{A^0} about $\varepsilon(R_i)$ to be negligible. The first and last terms on the right-hand side of this expression are, respectively, the slope of the A^0 potential curve and the R_i distribution in the initial state.

On the basis of symmetry arguments alone,[21,34] the matrix element for the electronic transition must clearly be dependent on the orientation of the molecular axis to the surface plane during the scattering event. This dependence has been observed in gas-phase charge exchange experments.[35] If little rotation occurs in the region near the surface where the occupation of the molecular state changes significantly, and this is indeed the case,[21] then (5) can be used to analyze an orientation angle and relative kinetic energy resolved experiment (where now P_{A^0} and $dN/d\epsilon$ are understood to be explicitly molecular orientation dependent). Such an experiment precisely defines the internuclear axis orientation existing throughout the duration of the capture event. The internuclear separation can be similarly defined if the vibrational motion is effectively frozen on the timescale of the capture event.

The aim of this and the accompanying paper is to determine P_{A^0} theoretically, including any molecular-axis-orientation dependences, and via (5) and (2), to calculate, respectively, the dissociation-product energy spectrum and bound-state vibrational population distribution.

B. Determination of the neutralization probability

In principal, P_{A^0}, the occupation or neutralization probability, contains contributions from both one-electron (resonant) and multielectron processes. Generalizing the arguments of Tully,[8] we find that in the adiabatic limit, if the discrete electronic states of the scattered molecule are uncoupled, or only weakly coupled, the amplitude a_i of the initial-state ion-channel i is described by the equation

$$\frac{da_i}{dt}=-\tfrac{1}{2}\Gamma_i a_i \,, \tag{6}$$

where Γ_i is an effective potential which results in leaking away of the amplitude a_i due to coupling with the metal conduction-band continuum states. This is (in atomic units), just equal to the neutralization rate ω_i.

If only one unoccupied molecular state couples strongly to occupied metal continuum states, we can integrate (6) over the elapsed time to obtain,

$$a_i(t)=a_i(-\infty)\exp\left[-\tfrac{1}{2}\int_{-\infty}^{t}\omega_i(t')dt'\right] , \tag{7}$$

where $a_i(-\infty)$ is the initial amplitude of the ion channel. The survival probability of the ith ion channel at time $t\rightarrow\infty$ is then

$$P_i'(\infty)=|\,a_i(\infty)\,|^2 \tag{8a}$$

$$=|\,a_i(-\infty)\,|^2\exp\left[-\int_{-\infty}^{\infty}\omega_i(t')dt'\right] \tag{8b}$$

and the neutralization probability or state occupation is

$$P_i(\infty)=1-P_i'(\infty) \,. \tag{9}$$

This, incidentally, is also the result one obtains by following a semiclassical rate-equation argument in the same limit.[9,36]

For a nondegenerate, two-state system (in the adiabatic limit), simple manipulation of (6), valid for each state, together with the definition (8a) leads to the coupled-rate equations

$$\frac{dP_i}{dt}=\omega_i(1-P_i-P_j) \,, \tag{10a}$$

$$\frac{dP_j}{dt}=\omega_j(1-P_j-P_i) \tag{10b}$$

describing the neutralization probabilities for each state. These equations were first derived to describe $2s,2p$ state occupations in atom-surface scattering by Hermann *et al.*,[37] using a classical argument. They can be solved numerically at $t=\infty$ for general ω_i and ω_j. Our problem therefore reduces to obtaining expressions for the transition probabilities along the scattering trajectory of each molecular state lying energetically below the Fermi level of the metal.

The transition probabilities referred to above describe all processes leading to decay of the initial hole state. These may be a combination of one and multielectron processes. In a related study of charge capture to low-energy protons at metal surfaces[38] we found the transition rates of one- and two-electron processes to exhibit almost identical time dependences. Assuming this result to be approximately true for molecules, a calculation of the resonant one-electron transition rates will act as a valuable guide to the time dependence of ω_i in (8b) and (10), and thus to the total occupation probabilities after scattering. Inclusion of all multielectron processes in the calculation of ω_i will clearly lead to quantitative adjustments to our results. We describe a method of determining the resonant transition rates for the molecule-metal interaction in the accompanying paper. The results we present below thus represent the charge capture probabilities corresponding to one-electron resonant processes, and provide a guide to the general features expected in the total charge capture probabilities.

III. RESULTS

We choose as a model system the $H_2{}^+$ aluminum interaction, for which the resonant transition probabilities for capture to the $X\,{}^1\Sigma_g^+$ singlet and $b\,{}^3\Sigma_u^+$ triplet states are calculated in II. The energetic position of these states with respect to the aluminum conduction-band density of states can be seen in Fig. 1. Ignoring possible image shifts, we observe that, at the equilibrium internuclear separation, the triplet and singlet states lie, respectively, 4 and 10 eV below the Al(110) Fermi level. Combining the maximum energy-level broadening (full width) calculated in II of 5 eV and an estimated image shift of 1 eV, we see that at room temperature, both states lie below empty states in the metal. As we shall demonstrate later, the charge transfer in fact occurs where the level width and shift are much smaller. Reionization cannot therefore occur, and the neutralization is described by the coupled differential equations (10), with i and j representing the singlet S and triplet T states, respectively.

We shall assume for convenience a linear incoming and outgoing scattering trajectory, approaching to within s_0 of the *electronic* surface (for the jellium description of aluminum used here, this is half a lattice constant above the surface layer of the nuclei). We also assume no energy loss (Fig. 3). Under these conditions, the perpendicular distance of the molecule center of mass above the surface at time t is, before scattering ($t<0$)

$$s=s_0-v_\perp t \; , \tag{11a}$$

and after scattering ($t>0$)

$$s=s_0+v_\perp t \; , \tag{11b}$$

where $v_\perp$ is the magnitude of the perpendicular component of the molecule velocity.

With the transformation (11a) and (11b), the differential equations (10a) and (10b) read (with the association $i=S$, $j=T$)

$$\frac{dP_S}{ds}=\frac{\omega_S}{\mp v}(1-P_S-P_T) \; , \tag{12a}$$

$$\frac{dP_T}{ds}=\frac{\omega_T}{\mp v}(1-P_T-P_S) \; , \tag{12b}$$

where the minus sign applies before scattering and the plus sign after scattering. These coupled equations must be integrated over the full trajectory to obtain $P_S(\infty)$ and $P_T(\infty)$, the singlet- and triplet-state occupations after scattering. This was performed using the resonant transition probabilities ω_S and ω_T from II, and results for the extreme cases where the molecular axis is perpendicular ($\alpha=0$) or parallel ($\alpha=90°$) to the surface are presented in Fig. 4.

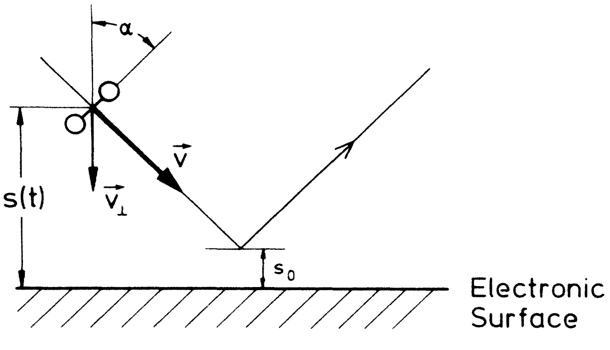

FIG. 3. Idealized trajectory for surface scattering. Specular reflection occurs since we assume zero energy loss during the collision.

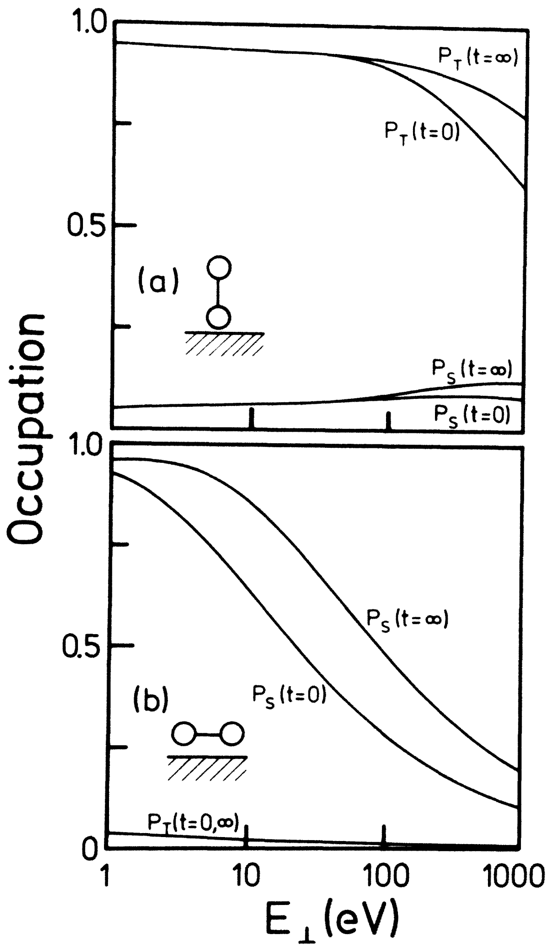

FIG. 4. Center-of-mass kinetic-energy dependence of the $H_2X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ state occupations for scattering of H_2^+ ($R_i=2$ a.u.) from Al(110). Plotted are the occupations at the turning point of the trajectory s_o (labeled $t=0$) and after scattering ($t=\infty$). (a) Perpendicular molecular-axis orientation to surface, $s_0=1$ a.u. (b) Parallel orientation, $s_0=0$ a.u. [the closest distance of approach of a proton to the surface in (a) and (b) is thus identical].

At low-incident energies ($E_\perp=\frac{1}{2}m_A v_\perp^2<10$ eV) essentially all incident H_2^+ molecules are neutralized. Almost all those scattered with molecular axes perpendicular to the surface dissociate via charge capture to the triplet state. Further, the charge transfer occurs on the incoming part of the trajectory. Molecules incident with molecular axes parallel to the surface are nearly all neutralized via charge capture to the singlet ground state. The probability of dissociation in this orientation lies below 5%. Once again the charge transfer occurs primarily on the incoming trajectory. The reason that the outgoing part of the scattering trajectory contributes little to the final charge state is easily seen by examining the behavior of the functions dP_S/ds and dP_T/ds, which represent the contribution of each section of the trajectory ds to the state occupations.[9,36] These functions are plotted in Fig. 5 for both singlet and triplet states. For $E_\perp=1$ eV, the most important contribution to the triplet occupation at perpendicu-

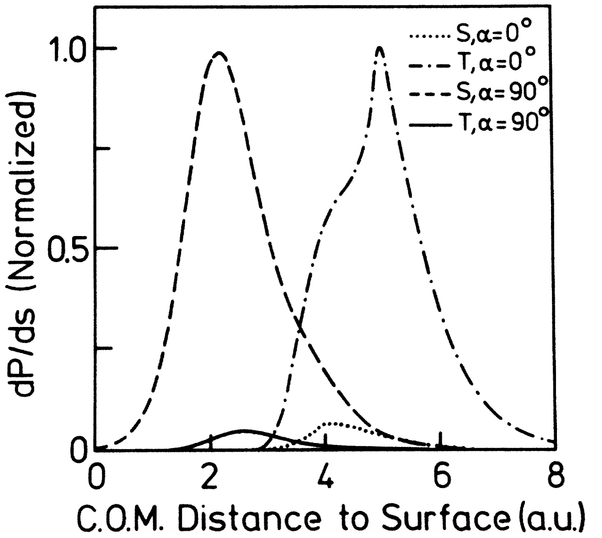

FIG. 5. Contribution of the interaction at distance s of the molecule center of mass (C.O.M.) from the surface to the final $X\,^1\Sigma_g^+(S)$ and $b\,^3\Sigma_u^+(T)$ occupations for $E_\perp = 1$ eV $H_2{}^+$ ($R_i = 2$ a.u.) scattering from Al(110). Results for parallel ($\alpha = 90°$) and perpendicular ($\alpha = 0°$) molecule-axis orientations to the surface are shown.

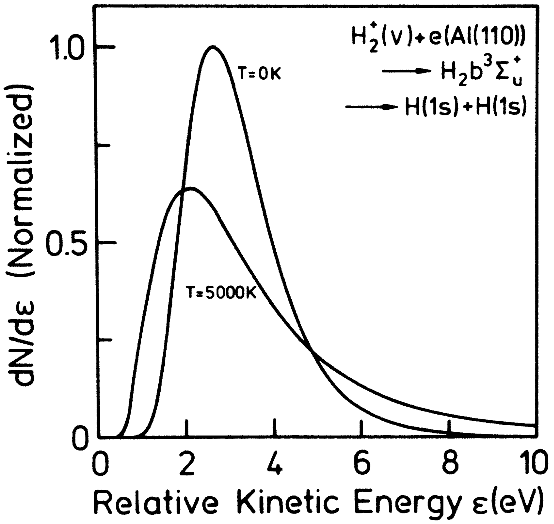

FIG. 7. Relative kinetic-energy distribution of dissociated H(1s) atoms following charge capture to the $b\,^3\Sigma_u^+$ state of H_2 during scattering of vibrationally excited $H_2{}^+$ beams with $E_\perp = 1$ eV from an Al(110) surface. The vibrational wave functions of the harmonic oscillator were used.

lar axis orientations occurs at a distance of 5.0 a.u. from the surface on the incident trajectory. At $E_\perp = 10$ eV this distance reduces to 3.4 a.u. In all cases, however, the electronic transition to the dissociating state occurs well before the molecule collides with the surface.

The situation for charge transfer to the singlet state at molecule-axis orientations parallel to the surface is similar. Here the peak neutralization rate lies at 2.2 a.u. for $E_\perp = 1$ eV, and at 1.8 a.u. for $E_\perp = 10$ eV. Thus for both orientations, the choice of closest distance of approach for the molecule trajectory is not important, nor is the error in the perturbation treatment of the interaction at small distances.

The more complex behavior seen in Fig. 4 at higher-perpendicular-incidence energies $E_\perp > 10$ eV would probably be difficult to investigate experimentally, since scattering at these energies results in significant rotational and vibrational excitation from momentum transfer alone.[21] The dependence on molecular-axis orientation of the probability for charge transfer to the singlet and triplet states, assuming an equilibrium-initial-internuclear separation in $H_2{}^+$ of $R_i = 2$ a.u. is presented in Fig. 6.

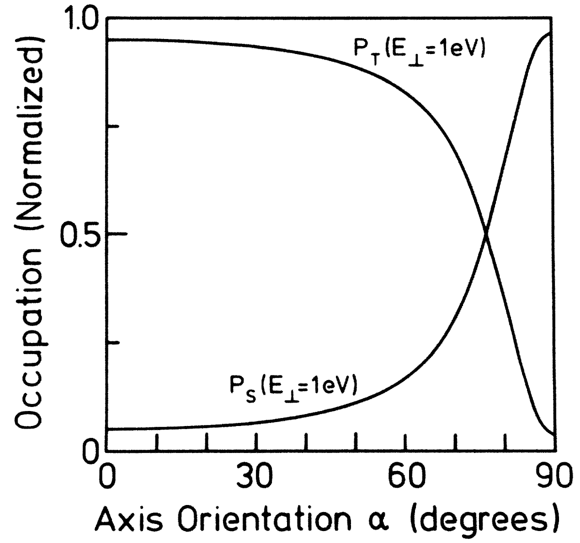

FIG. 6. Dependence on molecular-axis orientation to an Al(110) surface at the instant of charge capture of the probability of exit in the $X\,^1\Sigma_g^+$ or $b\,^3\Sigma_u^+$ channels, assuming an initial internuclear separation in $H_2{}^+$ of $R_i = 2$ a.u., and $E_\perp = 1$ eV.

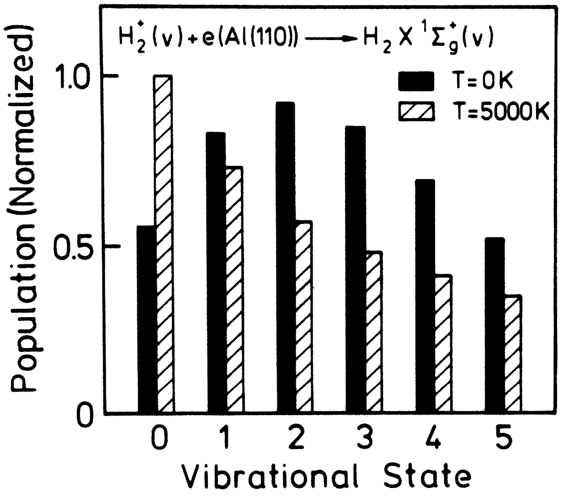

FIG. 8. Vibrational population distribution arising from charge transfer to the $X\,^1\Sigma_g^+$ state of H_2 during scattering of vibrationally excited $H_2{}^+$ beams with $E_\perp = 1$ eV from an Al(110) surface. Vibrational wave functions of the harmonic oscillator were used.

The weak dependence of ω_S and ω_T on ionization energy means that these dependences should approximate well those expected for vibrationally thermally excited H_2^+ beams scattered from aluminum.

Electron transfer to the triplet state of H_2 results in dissociation with an energy spectrum in center-of-mass coordinates described by (5). Its form, for H_2^+ vibrational temperatures of 0 and 5000 K, and $E_\perp = 1$ eV is shown in Fig. 7. The remaining part of the scattered neutral beam, arising from electron transfer to the singlet $X\,^1\Sigma_g^+$ state of H_2 with probability described by (2), has the vibrational population distribution plotted in Fig. 8.

The above orientation, energy, and vibrational distributions are readily accessible experimentally using the established techniques of translational spectroscopy[39] and laser-induced fluorescence.

IV. SUMMARY

We have provided a parameter-free model of the electronic interaction of a simple diatomic-molecular ion (H_2^+) with a jelliumlike metal surface [Al(110)]. Using resonant transition rates calculated in the accompanying paper, the general characteristics of the charge transfer to the lowest-lying singlet $X\,^1\Sigma_g^+$ and triplet $b\,^3\Sigma_u^+$ states of H_2 were investigated. For low-incident velocities ($E_\perp = \frac{1}{2}mv_\perp^2 < 10$ eV), capture to both states occurs on the incident portion of the scattering trajectory. Capture occurs primarily to the singlet state for molecule-axis orientations near parallel to the surface, and to the triplet state for orientations normal to the surface. This behavior has its origin in the antisymmetric character of the triplet-state electronic wave function.

Provided experimental conditions can be chosen which minimize the change in molecular-axis orientation during scattering, this orientation effect is directly measurable using coincidence techniques. The anticipated angular dependence of the $b\,^3\Sigma_u^+$ state occupation is explicitly calculated, as is the dissociation-fragment relative kinetic-energy distribution. Such an energy distribution, corresponding, however, to H_2^+ scattering on a Ni(111) surface, has already been published.[21]

Our calculations predict the vibrational population distribution for the singlet $X\,^1\Sigma_g^+$ state of H_2 resulting from charge capture. It would be interesting to test these predictions under experimental conditions where little vibrational excitation or relaxation occurs via momentum transfer or hole-pair creation during scattering.[21]

ACKNOWLEDGMENTS

One of us (K.J.S.) wishes to thank the Department of Physics and Astronomy, Vanderbilt University for providing the opportunity to complete aspects of this work. This project is supported in part by the Deutsche-Forschungsgemeinschaft.

---

[1] J. R. Hiskes and A. M. Karo, J. Appl. Phys. **56**, 1927 (1984).

[2] J. R. Hiskes and A. M. Karo, in *Production and Neutralization of Negative Ions and Beams,* Proceedings of the 3rd International Symposium, Brookhaven, 1983, AIP Conf. Proc. No. 111, edited by K. Prelec (AIP, New York, 1984), p. 125.

[3] E. H. A. Granneman, J. J. C. Geerlings, J. N. M. Van Wunnik, P. J. Van Bommel, H. J. Hopman, and J. Los, in *Production and Neutralization of Negative Ions and Beams,* Brookhaven, 1983, Ref. 2, p. 206.

[4] J. W. Gadzuk, Surf. Sci. **6**, 133 (1967); **6**, 159 (1967).

[5] A. Blandin, A. Nourtier, and D. W. Hone, J. Phys. (Paris) 369 (1976).

[6] M. Remy, J. Chem. Phys. **53**, 2487 (1970).

[7] W. Brenig, Z. Phys. **267**, 201 (1974).

[8] J. Tully, Phys. Rev. B **16**, 4324 (1977).

[9] A. D. Hagstrum, in *Inelastic Ion-Surface Collisions,* edited by N. H. Tolk, J. C. Tully, W. Heiland, and C. W. White (Academic, New York, 1977), p. 1.

[10] W. Bloss and D. Hone, Surf. Sci. **72**, 277 (1978).

[11] S. Horiguchi, K. Koyama, and Y. H. Ohtsuki, Phys. Status Solidi B **87**, 757 (1978).

[12] G. Doyen, Surf. Sci. **117**, 85 (1982).

[13] C. A. Moyer and K. Orvek, Surf. Sci. **114**, 295 (1982); **121**, 138 (1982).

[14] D. M. Newns, K. Makoshi, R. Brako, and J. N. M. van Wunnik, Phys. Scr. **T6**, 5 (1983).

[15] J. N. M. van Wunnik and J. Los, Phys. Scr. **T6**, 27 (1983).

[16] W. Eckstein, H. Verbeek, and S. Datz, Appl. Phys. Lett. **27**, 527 (1975).

[17] W. Heiland, U. Beitat, E. Taglauer, Phys. Rev. B **19**, 1677 (1979).

[18] B. Willerding, W. Heiland, and K. J. Snowdon, Phys. Rev. Lett. **53**, 2031 (1984).

[19] K. J. Snowdon and W. Heiland, Z. Phys. **318A**, 275 (1984).

[20] K. J. Snowdon, in *Desorption Induced by Electronic Transitions, DIET II,* edited by W. Brenig and D. Menzel (Springer, Berlin, 1985), p. 116.

[21] K. J. Snowdon, B. W. Willerding, and W. Heiland, Nucl. Instrum. Methods B **14**, 467 (1986).

[22] A. R. Burns, Phys. Rev. Lett. **55**, 525 (1985).

[23] I. S. Bitenski and E. S. Parilis, Nucl. Instrum. Methods **230B**, 364 (1984).

[24] I. S. Bitenski and E. S. Parilis, Surf. Sci. **161**, L565 (1985).

[25] K. J. Snowdon, R. Hentschke, W. Heiland, and P. Hertel, Z. Phys. **318A**, 261 (1984).

[26] P. Sigmund, H. M. Urbassek, and D. Matragrano, Nucl. Instrum. Methods B **14**, 495 (1986).

[27] R. Walkup, Ph. Avouris, and D. E. Harrison, Jr., Nucl. Instrum. Methods B **14**, 461 (1986).

[28] T. Darko, D. A. Baldwin, N. Shamir, J. W. Rabalais, and P. Hochmann, J. Chem. Phys. **76**, 6408 (1982).

[29] P. Hochmann, M. A. Miller, and J. W. Rabalais, J. Phys. Chem. **89**, 2751 (1985).

[30] P. Feibelman, Surf. Sci. **160**, 139 (1985).

[31] U. Imke, K. J. Snowdon, and W. Heiland, following paper, Phys. Rev. B **34**, 48 (1986).

[32] T. E. Sharp, At. Data **2**, 119 (1971).

[33] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).

[34] G. H. Dunn, Phys. Rev. Lett. **8**, 62 (1962).

[35] D. P. de Bruijn, J. Neuteboom, V. Sidis, and J. Los, Chem. Phys. **85**, 215 (1984).

[36] E. G. Overbosch, B. Rasser, A. D. Tenner, and J. Los, Surf.

Sci. **92**, 310 (1980).

[37] J. Hermann, J. Gehring, H. Schall, and V. Kempter , in *Desorption Induced by Electronic Transitions, Diet II,* Ref. 20, p. 266.

[38] K. J. Snowdon, R. Hentschke, A. Närmann, and W. Heiland, Surf. Sci. (to be published).

[39] D. P. de Bruijn and J. Los, Rev. Sci. Instrum. **53**, 1020 (1982).