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H⁺ PRODUCTION ON ALKALI-COATED SURFACES

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FORMATION PROCESSES AND SECONDARY EMISSION COEFFICIENTS
FOR H^+ PRODUCTION ON ALKALI-COATED SURFACES*

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Abstract

The formation of negative ions by hydrogen collisions on cesium-coated surfaces is discussed in the limiting cases where the resident cesium is either in the purely ionic state or in the purely atomic state. The survival fraction for negative ions moving away from a metal surface is calculated using a method employing complex eigenvalues. The fraction of surviving ions is found to be larger than calculated by previous workers. The secondary emission coefficient for negative ion production by incident atoms with energies of ten to one hundred electron volts is estimated to be in the range thirty to fifty per cent. The secondary emission coefficient is found to be a sensitive function of the thickness of the alkali adsorbate coating for ion energies in the range below a few hundred electron volts.

1. Introduction

Low energy protons incident upon metallic surfaces are backscattered from the surface with efficiencies of from fifty to ninety per cent. Upon emerging from the crystal lattice these ions are efficiently neutralized by Auger processes while still within distances of several angstroms from the surface.² For an alkali-coated metal substrate and at still larger distances these atoms are in turn converted to negative ions by electrons transferred from near the top of the Fermi level.³ At the present time, experimental data on backscattering yields for hydrogen below one kev incident energy are very scant, but one suspects that the final charge state of the reflected particle will be only weakly dependent upon the incident charge state. The fraction of incident particles reflected as negative ions can be considered to be the product of three factors: the backscattered fraction of incident particles reflecting off the metal lattice; the probability of conversion of hydrogen to a negative ion during the collision; and the probability of a negative ion surviving as it moves away from the metal surface. For purposes of interpreting the behavior of surface-plasma sources, this product is required over the range of incident particle energies from near threshold, about one electron-volt, up to several hundred electron volts.

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II. Formation of Negative Ions

A mechanism for the formation of negative ions by energetic hydrogen atoms incident upon tungsten surfaces with partial monolayer coverages of alkali atoms has been discussed in an earlier paper.³ In that paper the alkali had been assumed to be residing on the surface in atomic form and the active electronic level during the surface collision was approximated as the sum of the cesium-hydride molecular levels and the image potential. The question of the charge state of cesium which occurs for partial monolayer coverages has been reviewed recently by Wojciechowski⁴ in the light of the jellium model results of Lang and Kohn.⁵ For partial monolayer coverages near the work function minimum the cesium is found to be principally in the atomic state. The lowering of the surface work function as a consequence of the electric dipole layer which arises from the cesium coverage does imply however that the cesium atoms carry a residual positive charge even at the work function minimum. This fact together with the continuing discussion centered about the charge state and its consequences for the negative ion formation process has prompted us to reconsider the formation process. Using the recently computed hydrogen atom-cesium ion potential interaction we can now discuss the negative ion formation in the limiting case where the cesium is purely ionic.

In Fig. 1 is shown the CsH molecular potentials including $Cs^+ + H$ interaction.⁶ The notable feature of this latter curve is its repulsive form at small internuclear separations. Notice however that the interaction potential is essentially constant up to rather small internuclear separations.

In Fig. 2 is shown a schematic energy diagram for the purpose of demonstrating the formation of negative ions by hydrogen atoms impinging on a surface layer of Cs^+ ions. The existence of the electric dipole layer arising from the ionized cesium layer reduces the effective surface work function by 3 eV to 1.52 eV at the work function minimum. An electron excited to 1.52 eV in the substrate can penetrate the dipole barrier and escape to infinity with zero potential and kinetic energy. The image plane is located 3.2 a_0 in front of the substrate well,⁷ with the cesium ion placed 1.9 a_0 in front of the image plane. (This position for the cesium ion is discussed in a

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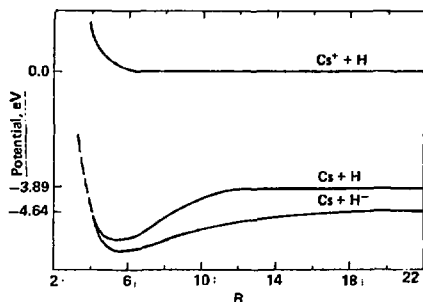


Fig. 1. Potential energy curves for the $\text{Cs}^+ + \text{H}$, CsH , and CsH^- molecular systems plotted as a function of the internuclear separation, R , measured in units of the Bohr radius, a_0 .

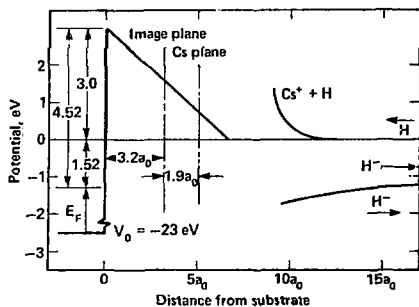


Fig. 2. Potential energy schematic illustrating the interaction of H and H^- with Cs^+ on a tungsten substrate. See text for details.

later paragraph.) The electronic energy level of an H^- ion located at great distances from the surface is given by the electron affinity, -0.754 eV. As the H^- ion approaches the surface it experiences an image potential, the sum of image potential plus affinity falling below the Fermi level a distance of $8.83 a_0$ in front of the image plane. A hydrogen atom approaching the surface on the other hand experiences no forces until it comes near a cesium ion, as in Fig. 1; thereafter its closest approach will depend upon its incident kinetic energy. Even for a one electron-volt atom however, this repulsive interaction does not prevent the atom from becoming sufficiently close to the surface that an H^- ion can form by an electron tunneling through from the substrate reservoir at energy E_F .

Using the available CsH molecular potentials, negative ion formation is energetically possible for the limiting cases of the surface cesium being either completely ionized or totally neutral.

III. Survival of Negative Ions Moving Away From the Surface

A negative ion moving away from the metal surface can lose its electron to the metal by barrier penetration once the separation is sufficiently large that the ion electronic level lies above the occupied electronic states of the metal. The transition probabilities for this loss mechanism have been calculated independently by Kishinevskiy⁸ and by Janev⁹ taking for the barrier the image potential. In general however, the potential barrier may be quite complex; in order to accommodate several terms in the potential we have employed a calculation of the transition probability which relies upon the method of complex eigenvalues. An earlier account of this work was presented at the Negative Ion Workshop in Moscow.¹⁰

The active electron in a system consisting of substrate, cesium layer, and negative ion can be described by the equation

$$-\frac{\pi}{\Gamma} \frac{\partial \psi}{\partial t} = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right\} \psi, \quad (1)$$

with the solution

$$\psi = \chi(\vec{r}) e^{-\frac{i}{\hbar} E t}. \quad (2)$$

Introducing the complex eigenvalue

$$W = E - \frac{i}{2} \Gamma, \quad (3)$$

the electron density becomes

$$|\psi|^2 = |\chi(\vec{r})|^2 e^{-\frac{\Gamma}{\hbar} t}. \quad (4)$$

At any point in space the electron density is seen to decay in time with a transition probability equal to Γ/\hbar .

Because of the granular nature of the surface an accurate description of the process would require, strictly speaking, a full three dimensional treatment. If we were to ignore this granular structure and consider instead a normal collision of hydrogen in-line with a surface cesium atom, the problem is reduced to two dimensions. As was first pointed out by Janev,⁹ the problem can be reduced in its essentials to a one dimensional calculation by introducing the parabolic coordinates

$$\begin{aligned} \zeta &= r + z, \\ \eta &= r - z, \\ \phi &= \phi. \end{aligned} \quad (5)$$

Upon setting the azimuthal quantum number equal to zero, expressing lengths and energies in units of Bohr radii and Rydbergs, respectively, and describing the negative ion by a coulomb state with effective charge Z and unperturbed energy level equal to Z^2 , the introduction of coordinates (5) into eq. (1) leads to an n equation

$$\frac{d^2 v}{dn^2} + \frac{1}{4} \left\{ W + V_0 + VI + \frac{2Z}{n} + \frac{1}{n^2} + \epsilon \eta + \frac{1}{\zeta - \eta - 2z_0} \right\} v = 0. \quad (6)$$

The term V_0 in the brackets is a uniform potential within the substrate; the term VI is a constant term equal to the surface work function and applicable in certain regions (see Figs. 3 and 5); the next two terms arise from the coulomb term and coordinate choice, respectively; the term with electric field coefficient occurs in those regions of uniform electric field; the last term in the brackets is the image term, with z_0 the z -coordinate of the image plane measured from the center of the negative ion. The separation of coordinates fails only in the case of the image term which contains the z coordinate explicitly. As Janev was the first to point out, $z \ll \eta$ in the range of integration, and by neglecting this coordinate in the image term we have effectively achieved a separation.

The function $v(n)$ is complex. Writing $v = u + iw$ and introducing into equation (6), we obtain a pair of coupled equations for the real and imaginary functions of v :

$$\begin{aligned} \frac{d^2 u}{dn^2} &= -\frac{1}{4} \left\{ \epsilon + VI + \frac{2Z}{n} + \frac{1}{n^2} + \epsilon \eta - \frac{1}{n + 2z_0} \right\} u - \frac{\Gamma}{8} w, \\ \frac{d^2 w}{dn^2} &= -\frac{1}{4} \left\{ \epsilon + VI + \frac{2Z}{n} + \frac{1}{n^2} + \epsilon \eta - \frac{1}{n + 2z_0} \right\} w + \frac{\Gamma}{8} u. \end{aligned} \quad (7)$$

We are interested in a solution of Eqs. (7) which represents a standing wave negative ion function in the negative ion region and a purely outgoing wave propagating in the region of the metal substrate. Referring to Eq. (6), within the substrate this equation reduces to

$$\frac{d^2 v}{dn^2} + \frac{1}{4} [W + V_0] v = 0, \quad (8)$$

with solution

$$\begin{aligned} v &= \exp i \left[(W + V_0)/4 \right]^{1/2} n, \\ v &= \exp \frac{i}{\sqrt{2}} \left\{ \left[\left(\frac{E + V_0}{4} \right) + \sqrt{\left(\frac{E + V_0}{4} \right)^2 + \left(\frac{\Gamma}{8} \right)^2} \right]^{1/2} \right. \\ &\quad \left. - i \left[-\left(\frac{E + V_0}{4} \right) + \sqrt{\left(\frac{E + V_0}{4} \right)^2 + \left(\frac{\Gamma}{8} \right)^2} \right]^{1/2} \right\} n. \end{aligned} \quad (9)$$

Equation (9) has the form required for a purely outgoing wave. Matching this solution to the interior solutions for u and w at the boundary of the substrate, the matching conditions become

$$\begin{aligned} \frac{u' u + w' w}{u^2 + w^2} &= \frac{1}{\sqrt{2}} \left[-\left(\frac{E + V_0}{4} \right) + \sqrt{\left(\frac{E + F}{4} \right)^2 + \left(\frac{\Gamma}{8} \right)^2} \right]^{1/2}, \\ \frac{u w' - w u'}{u^2 + w^2} &= \frac{1}{\sqrt{2}} \left[\left(\frac{E + V_0}{4} \right) + \sqrt{\left(\frac{E + F}{4} \right)^2 + \left(\frac{\Gamma}{8} \right)^2} \right]^{1/2} \end{aligned} \quad (10)$$

The integration procedure consists of selecting a negative ion separation distance z_0 , and searching for values of E and Γ which satisfy the conditions (10). The resulting value for Γ gives the transition rate, Γ/π , at that separation distance. The rate of loss of electron density is, from (4),

$$\frac{d|\psi|^2}{dt} = -\frac{\Gamma}{\pi} |\psi|^2. \quad (11)$$

the loss rate Γ/π is a function of separation distance z_0 ; writing $dt = dz_0/v$, where v is the H^- ion velocity as it moves away from the surface, the fraction of H^- ions surviving the electron loss to the substrate becomes

$$f = \exp - \int_{z_1}^{\infty} \frac{\Gamma}{\pi} \frac{dz_0}{v}. \quad (12)$$

The starting point for the integrations, z_i , begins at the point where the active electronic energy level rises above the filled electronic states of the substrate. At very low H^+ ion energies the ion is slowed as it leaves the surface because of the increasing electronic energy. If $V(z_0)$ is the electronic potential (taken equal to zero at infinity) the correct expression for the velocity is

$$v = \left[v_f^2 - \frac{2}{m} V(z_0) \right]^{1/2}, \quad (13)$$

where v_f is the asymptotic velocity. The transition rates have been calculated for several surface geometries. In the tradition of the Kishinevskiy-Janev calculations, we consider first only an image barrier. Taking the surface in the negative z direction measured from the ion, with ϕ the surface work function, the potential distribution is taken to be

$$V = V(\text{image}) = \frac{e^2}{4a_0} \frac{1}{z_0 - z}, \quad z_B = z_0 - \frac{e^2}{4a_0\phi} < z < 0;$$

$$V = V_0, \quad z < z_B \quad (14)$$

Using values $\phi = 1.52$ eV and $V_0 = 23$ eV appropriate to tungsten,¹¹ we noticed that as the H^+ ion was brought up to z_0 the real part of the eigenvalue, Γ , at first became more negative as expected, but then reversed and increased in value. The increase in eigenvalue is attributed to a necessary increase in eigenfunction curvature required to satisfy the boundary conditions (10). Physically, this problem has its origin in the assumption that formation and loss mechanisms can be separated. This is only possible provided $\Gamma \ll E$.

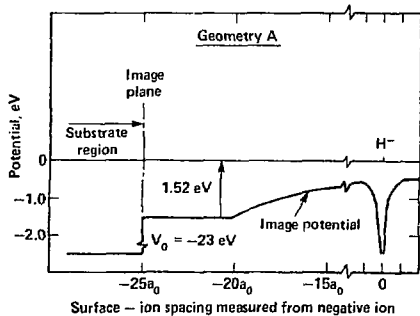


Fig. 3 Potential energy schematic for Geometry A. See text.

Bearing in mind that jellium model results place the image plane well out in front of the substrate nuclei,⁷ we next selected the surface geometry shown in Figure 3, which includes a constant potential region separating the image and substrate regions, but still in the spirit of the Kishinevskiy-Janev potentials. The survival fraction is shown in Figure 4 as a function of the backscattered H^+ energy and compared with the Kishinevskiy fractions. The fractions calculated here are larger than those of Kishinevskiy⁸ but differ by factors of less than two for energies above 2 eV.

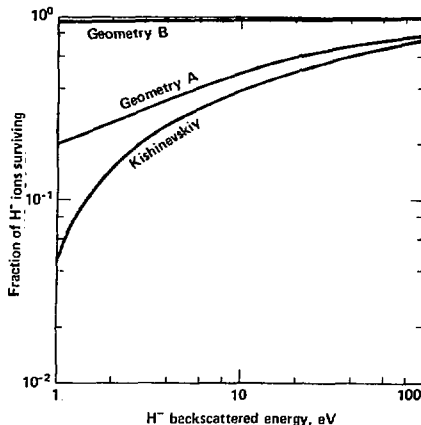


Fig. 4 The survival fraction, f , as a function of the asymptotic H^+ backscattering energy.

The existence of an electric dipole layer at the surface reduces the probability of barrier penetration from the negative ion into the substrate. In Fig. 5 is drawn the potential taking into account the electric dipole layer, which is included here as a region of uniform electric field, \mathcal{E} , across which the potential drop equals 3.0 eV, the amount of reduction of surface work function at the work function minimum. The potential shown in the figure is based upon the following considerations: The zero of the potential is chosen equal to the potential energy of an electron at infinity. An electron excited in the substrate to 1.52 eV above the Fermi level can penetrate the dipole layer and escape to infinity. The image plane is situated in front of the substrate a distance prescribed by Smith, Lang, and Kohn.⁷ The position of the cesium plane is suggested by the experimental data of Anderson and Kasemo.¹² The width of the dipole layer is consistent with the radius of the Cs ion, $1.6 a_0$. The barrier inside the image plane

is introduced to account for the saturation of the image effect close to the substrate.

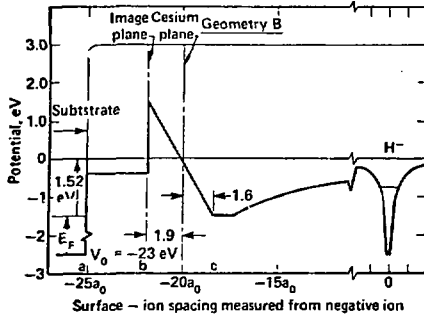


Fig. 5 Potential energy schematic for Geometry B. See text.

The transition probabilities for this geometry are appreciably less than for the former, and the survival fraction is near unity even for low energy ions, Fig. 4.

IV. Conversion of Hydrogen Atoms to Negative Ions

We discuss next the probability of converting a hydrogen atom to a negative ion during the course of the surface collision. Referring again to Figure 5, the limiting process for electron capture by the atom is the barrier penetration from the substrate at a through the region of the dipole layer to a point c by an electron initially near the top of the Fermi level. We can estimate the transition probability for this process using the appropriate HKB formula: (neglecting reflection at the inner step at b)

$$P = \gamma \exp - \left\{ 2 \sqrt{\frac{2m}{\hbar^2}} \int_a^c \sqrt{V - E} dz_0 \right\} \quad (15)$$

A reasonable value for the frequency factor, γ , for electrons in the substrate is 10^{16} sec^{-1} . Denoting by V_1 the height of the potential at the edge of the substrate well and by V_2 the peak height, and using the dimensions shown in the figure, the formula (15) easily integrates to

$$P = \gamma \exp - 2 \sqrt{\frac{2m}{\hbar^2}} \left\{ 3.2 a_0 \sqrt{V_1} + \frac{7}{3} a_0 \sqrt{V_2} \right\} \\ = 2 \times 10^{14} \text{ sec}^{-1} \quad (16)$$

The probability for negative ion formation is

$$P_- = 1 - e^{-P\tau} \quad (17)$$

where τ is the rollout time during which the energy level of the active electron lies below the Fermi level. From Ref. 3, formation is expected to occur over a distance of about $10 a_0$, giving $\tau = 10 a_0/v$. At the higher velocities formation is less probable, a trend which counteracts the trends for the survival fraction, f . For a 100 eV H⁺ ion, $P_- \approx 55\%$, increasing to $P_- \approx 99\%$ at 1 eV. These estimates indicate that the formation probability is more limiting than the survival fraction and suggests this problem warrants a more careful study.

The calculations of Oen and Robinson¹ indicate backscattering particle reflection coefficients, R_N , to be in the range 60% to 80% for incident hydrogen particles in the energy range from ten to one hundred electron volts and for scattering off transition-element crystals. Combining these reflection coefficients with the other factors computed in this paper, we can estimate the overall secondary emission coefficient, $\kappa = R_N P f$, to be in the range 30% to 50% for incident particle energies in the range 10 to 100 eV. No information exists on reflection coefficients (or alternatively, sticking coefficients) down to the one electron-volt range, but the product $P f$ indicates an upper limit for the secondary emission coefficient of order unity.

In a later paper at this Symposium, Schneider et al.¹³ report the secondary emission coefficients for hydrogen ions incident upon metal substrates with thick alkali coatings, i.e. many monolayers. Under these conditions the reflection coefficients are presumably determined by the alkali coating rather than the substrate. More important, the alkali coating is now a conductor and electrons can be lost from the negative ion directly to the alkali adsorbate and do not have to penetrate the dipole layer in order to be absorbed by the surface. In this case the survival fraction is reduced considerably compared to the survival fraction calculated for a part¹ monolayer alkali coating.

To treat this case we have used Geometry A but with the work function taken equal to the bulk work function for cesium or potassium, 1.9 eV or 2.25 eV, respectively. For these larger work functions the condition $\Gamma \ll E$ does not hold close to the surface and the broadened level overlaps the Fermi level even when E is substantially less than the work function. The starting point for the integrations, z_i in Eq. (12), is then ambiguous; this difficulty is intrinsic to any such calculation in which the formation probability and destruction probability (survival fraction) are treated independently. Here we have arbitrarily chosen z_i to be the position at which

the area under the broadened energy level overlaps the Fermi level by 30%, i.e. where $\phi = E + 0.981\Gamma$, with ϕ the surface work function.

The results of these calculations are shown in Fig. 6 and compared with the partial cesium monolayer results calculated using Geometry B, Fig. 5. The thick coverage alkali targets have substantially lower survival fractions, and as a consequence the secondary emission coefficients will show a substantial decrease below 100 eV. The only prospects for maintaining a large secondary emission coefficient at low energies rests with the application of the partial monolayer coverage.

The survival fractions shown in Fig. 6 have been calculated for normal emission of negative ions; substantial emission at angles away from the normal will cause the curves in the figure to be more dispersive.

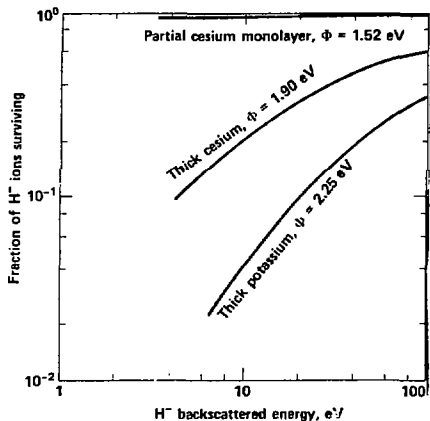


Fig. 6 Survival fractions for thick coatings of cesium and potassium compared with the fraction for a partial cesium monolayer.

V. Conclusions

A mechanism for negative ion production by hydrogen atoms on minimum-work-function cesium-coated surfaces has been demonstrated for the limiting cases of the cesium resident on the surface in a purely ionic or purely atomic form. The overall secondary emission coefficients for incident hydrogen atoms or ions in the range from ten to one hundred electron volts are estimated to be in the range 30% to 50%. At the lower energies the survival fractions are found to be larger than those calculated by other workers. In the case of thick alkali coatings on metal substrates the

secondary emission coefficient is substantially reduced at energies below 10. eV compared with the coefficient for a partial-monolayer cesium coating.

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