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ATOMIC AND MOLECULAR SURFACE AND VOLUME PROCESSES IN THE ANALYSIS OF NEGATIVE HYDROGEN DISCHARGES

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Abstract

The generation of hydrogen negative ions in hydrogen discharges is due to a combination of electronic excitation and wall relaxation processes. Principal processes are energetic electron excitation to form $H_2(\nu'')$, followed by low-energy electron dissociative attachment to form $H^- + H$. Wall recombination of H_2^+, H_3^+ ions are also a source of $H_2(\nu'')$.

We consider the formation of $H_2(\nu'')$ and H^- by H_2^+ and H_3^+ ions incident upon metal surfaces.[1] A four-step model for incident $H_2^+(\nu)$ recombination and dissociation proceeds via: (1) Electric dissociation of high ν ions in the image field ultimately producing atomic dissociation fragments; (2) resonant capture to form $H_2(b^3\sum_u)$ and $H_2(X\ {}^1\sum_g, \underline{\nu}'')$, with b dominant over X in ratio 69:31; (3) Auger relaxation of b to X to contribute to the $H_2(X\ {}^1\sum_g, \underline{\nu}'')$, yield; (4) $H_2(\underline{\nu}'')$ drift to surface to experience "hard" nuclear collision and form final population distribution, $H_2(\nu'')$, and final dissociation products.[1] Experimental H_2/H yields are consistent with four-step ratio, not consistent with single-step singlet-model ratio, and imply rapid Auger relaxation following b-state capture. Final vibrational distributions reported here differ markedly from earlier calculated distributions. Level shifts due to image effects cause H_2 n = 2-parentage capture to be marginally accessible for barium surfaces ($\phi = 2.7$ eV) but quite possible for cesium ($\phi = 2.14$ eV) and Cs/Mo ($\phi \approx 1.6$ eV) surfaces. Predissociation of $H_2(c^3\Pi_u)$ competes with Auger relaxation but predissociation times are too long to allow significant H_2 dissociation.

Opposing image shifts of $H_2^-({}^2\sum_u)$, $H_2(X^1\sum_g)$ allow direct H^- formation from $H_2(\nu'')$ by rebounds from Ba, Cs, Cs/Mo surfaces. H^- yields are evaluated explicitly for Ba surfaces.

For H_3^+ incident: (1) Small (2%) electric dissociation to $H^+ + H_2$; (2) resonant capture to $2p\,{}^2E' \rightarrow {}^2A_1, {}^2B_2$ states; (3) drifting $H_3(\nu''')$ in ${}^2A_1$ ground electronic state dissociates into H_2+H to provide $H_2(\underline{\nu}'')$ distribution; (4) hard collision of drifting $H_2(\underline{\nu}'')$ produces final distribution $H_2(\nu'')$. Final vibrational distributions from H_2^+ and H_3^+ are compared. Low work function surfaces allow capture into $H_3(2s\ {}^2A_1')$ and $H_3(2p\ {}^2A_2'')$ states. Vibrational and rotational couplings, respectively, couple

these states to $2p\ ^2A_1$ to allow predissociation to yield $H_2(\nu'') + H$. The lowest vibrational level of $2s\ ^2A_1'$ is too long-lived (1.8×10^{-13} sec.) to compete favorably with Auger relaxation to $2p\ ^2E'$, but predissociation lifetimes may shorten for higher vibrational levels, analogous to $H_2(\mathrm{c}\ ^3\Pi_u)$, to provide a final $H_2(\nu'')$ distribution, that is distinct from that obtained from $H_3(2p\ ^2E')$ resonant capture.[2] The lifetime of $2p\ ^2A_2''$ against predissociation appears to be too long, $10^{-11} - 10^{-13}$ sec, to be competitive with Auger relaxation. $H_3(n = 3)$ states can be accessed only with very low work function surfaces, $\phi < 1.5$ eV. But predissociation times appear to be excessively long compared with Auger relaxation to allow one to access the broad H_2 vibrational distributions observed[3] in the predissociation of the $3s\ ^2A_1'$, and $3d\ ^2E''$ states.

I. Introduction

The principal source of negative ion generation in hydrogen discharges is now recognized to be low-energy electron attachment to $H_2(\nu'')$ molecules excited to the middle portion of the vibrational spectrum.[4] Electron excitation processes are generall taken to be the principal source of $H_2(\nu'')$ generation,[5] with high-energy excitations through the singlet spectrum being the principal excitation process populating the active portion of the vibrational spectrum. A description of the collisional re-excitation from level $\underline{\nu}''$, to level ν'', requires a 15×15 matrix of cross sections linking all initial and final levels. These cross sections have been evaluated and incorporated into the modelling code.[6]

An additional source of vibrational excitation may be derived from recombination of H_2^+ and H_3^+ ions on the surfaces of the discharge. In this case the molecular ions will impinge with kinetic energies given by the plasma potential, 1–10 eV. In this paper we report the evaluation of the $H_2(\nu'')$ resulting from the surface recombination process.

The use of low-work-function materials for the discharge surfaces makes possible two additional source of negative ions: the direct formation of negative ions by hydrogen atoms rebounding from the surface, and the dissociation of H_2^- ions formed in the surface selvage. In a recent paper van Os et al.[7] have demonstrated the efficacy of Ba surfaces as an active medium for H^- formation. Here we shall extend our discussion to H_2^+, H_3^+ collisions on Ba surfaces and inventory the generation of H, $H_2(\nu'')$, and H^- rebounding from these surfaces.

II. Surface Recombination and Dissociation of H_2^+ and H_3^+ ions

The surface recombination of H_2^+ and H_3^+ proceeds through a four-step model outlined earlier.[1] We shall summarize briefly the H_2^+ problem: (1) the initial populations, $p(\nu)$, of the $H_2^+(\nu)$ vibrational level $\nu = 18, 17, 16, \ldots$, are successively quenched as the image field electrically dissociates the incoming H_2^+ ion. (2) Resonant electron capture from the surface forms $H_2(b^3\sum_u)$ halting any further electric dissociation. (3) Almost immediately, i.e. with a rate comparable to the resonant capture rate, Auger relaxation relaxes the repulsive b state to form the ground electronic state, $H_2(X'\sum_g)$. With some lesser probability resonant capture occurs directly to the singlet ground state.[8] The final vibrational distributions for the ground state formed by transitions through each of these channels is illustrated in Ref. 10.

In the fourth step (4) molecules in these distributions strike the surface and undergo a "hard" nuclear collision,[9] rebounding to form the final distribution, $H_2(\nu'')$. This distribution, for 10 eV incident $H_2(\nu'')$ molecules and taken from a forthcoming paper,[10] is shown in Fig. 1.

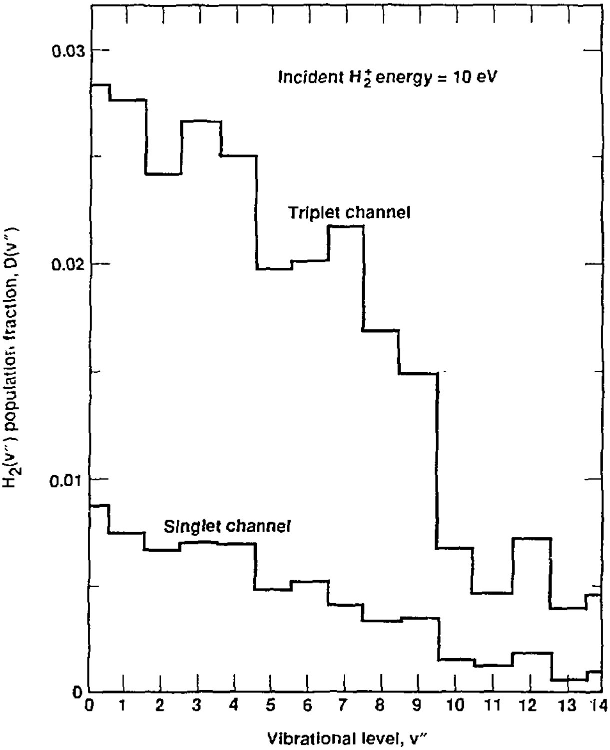

Figure 1: Final population distribution, $H_2(\nu'')$, per incident 10 eV H_2^+ ion.

The $H_3^+(\nu''')$ recombination for conventional metals with work functions $\phi > 4.5$ eV proceeds through the $2p\ ^2E' \rightarrow 2p\ ^2A_1$ state to yield $H_2(\nu'') + H$. The $H_2(\nu'')$ distribution is obtained by projecting the initial population of ν''' on the H_3^+ potential surface[11] onto the H_3 surface,[12] followed by a projection onto the $H_2(\nu'')$ plane.[10] This $H_2(\nu'')$ in turn undergoes a "hard" collision to provide the final $H_2(\nu'')$ distribution shown in Fig. 2.

Inspection of the distribution here for $\nu'' > 5$ and comparing with final H_2^+ distributions[10] shows that the H_3^+ ion is a more useful ion for negative ion generation than is H_2^+.

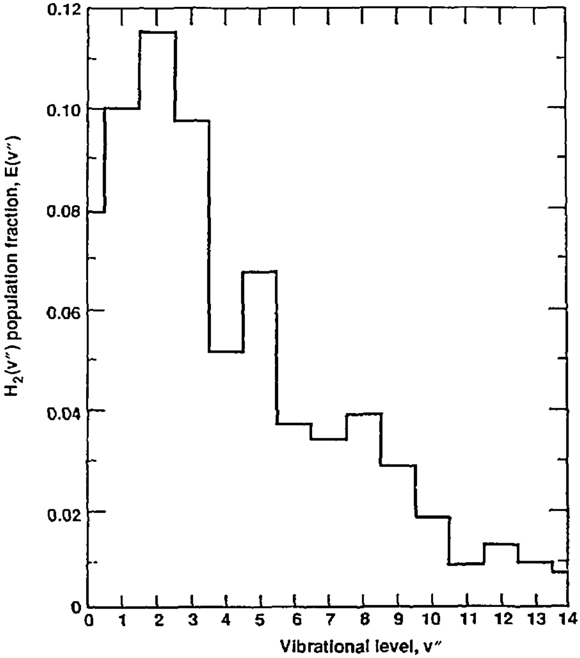

Figure 2: Final population distribution, $H_2(\nu'')$, per incident 6 eV H_3^+ ion.

III. Molecular Ion Collisions with Low Work-Function Surfaces

Molecular ion collisions with low work-function surfaces will allow for resonant captures into higher electronic states. These captures in turn will be Auger relaxed to provide an additional contribution to the ground state vibrational distribution. Low work-function collisions also allow for two additional mechanism for negative ion generation: Direct H^- production by electron capture to H atoms backscattering from the surface, and H^- production by dissociation of H_2^- ions formed from rebounding $H_2(\nu'')$ moving outward through the surface selvage.

The generation of H^- ions by H^+, H incident upon barium surfaces has been characterized experimentally by van Os et al.[7] In Fig. 3 their data is re-plotted for comparison with the product function

$$N(-) = a(H)[1 - \exp - \nu_\perp/\nu_\perp^o] . \tag{1}$$

plotted against the outgoing perpendicular velocity component, $\nu_\perp$.

From this figure the asymptotic dependence on $\nu_\perp$ indicates a formation probability, $a(H)$, equal to 0.3; the survival probability, given by the bracketed factor, remains as large as 0.33 for perpendicular energy components as low as 2.0 eV.

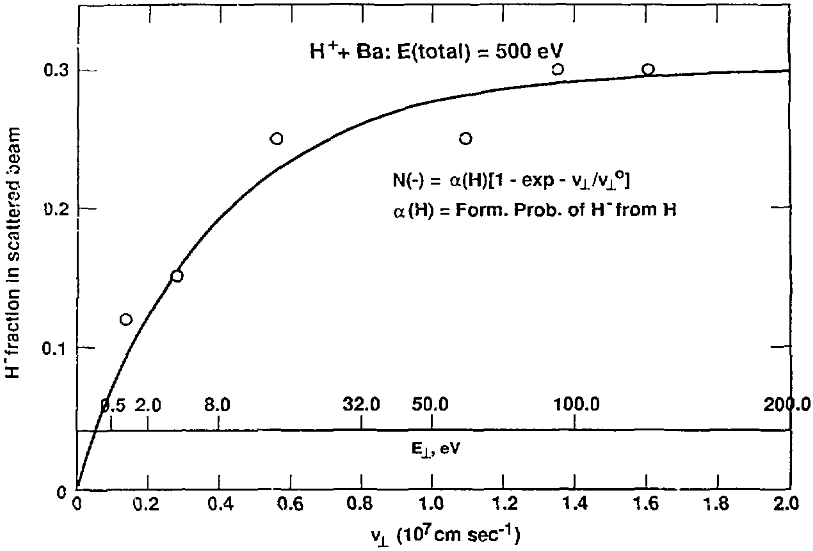

Figure 3: H^- generation vs outgoing normal velocity or energy, Eq. 1.

In general one expects the energy level of a neutral atomic or molecular system to be raised as it experiences an increasing image field. Bruch and Ruijgrok[13] have shown however, that there is an insignificant level shift for image-plane separations $z - z_o > 3a_o$, the range where resonant electron capture would be expected to occur. For the downward shift of the negative ion level we use the expansion,

$$\Delta E = -\frac{1}{4}\frac{1}{z - z_o} - \frac{1}{2!}\alpha\frac{1}{16(z - z_o)^4} - \frac{1}{4!}\beta\frac{1}{256(z - z_o)^8} + \dots \quad (2)$$

The dipole and quadrupole polorizabilities, α, β for H^- are 215.5 and 7765.0, respectively.[14,15] No information is available for the polarizability of the H_2^- ion, but in a first approximation the H_2^- configuration is an $H^- + H$ configuration from the level crossing outward, and for this discussion we shall approximate the H_2^- level shift by Eq. (2) and using the H^- polarizabilities.

The energetics of the barium $-H_2^-$, $H_2(\nu'')$ system is illustrated isometrically in Fig. 4 where is shown the energy variations as a function of image-plane separation and internuclear separation. The relative positions of the H_2^-, $H_2(\nu'')$ potentials are shown in the right hand plane for infinite surface-molecule separation. At this separation the H_2^- level lies too high to allow resonant capture from the barium ($\phi = 2.7$ eV) to $H_2(\nu'')$ to form H_2^-.

At an image-plane molecule separation of 3.2 a_o the H_2^- configuration has shifted downward with respect to $H_2(\nu'')$ such that the asymptotic H_2^- potential lies as low as the $H_2(\nu'' = 0)$ level. At this separation resonant electron capture can occur from the barium to levels $\nu'' = 0, 1, 2$, and 3 of H_2, resulting in H_2^- dissociation into $H^- + H$.

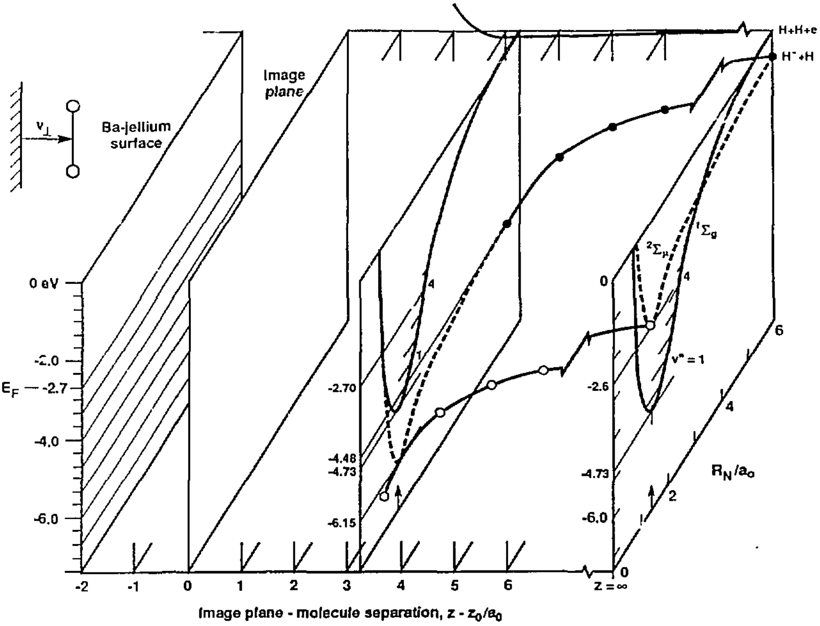

Figure 4: Energetics of the barium H_2^-, $H_2(\nu'')$ system.

We can now summarize the resonant capture possibilities for a 6 eV incident H_3^+ ion rebounding as 4 eV $H_2(\nu'')$ and 2 eV H fragments. In the initial recombination process 20% of the H_3^+ leads to $3H$ dissociation 80% and to $H + H_2$ to give a yield[16] of $1.4H/H_3^+$. From the van Os data of Fig. 3 we conclude that 10% of these atoms will appear as H^- ions to give $0.14H^-/H_3^+$.

From Ref. 10 we have that 32% of the rebounding $H_2(\nu'')$ are in levels $\nu'' = 0$, 1, 2, and 3, and these molecules are subject to H_2^- formation and dissociation in their flight from $z - z_o = 2$ to 3.2 a_o. From Fig. 3 we find that 0.33 of these H^- survive to give an additional 0.10 H^-/H_3^+. The remaining flux is then 0.54 H/H_3^+. For those $H_2(\nu' > 3)$, representing a fraction 0.48 H_2/H_3^+, no resonant capture to form H_2^- can occur.

One can now take inventory of the subsequent capture and dissociation processes for 6.0 eV incident H_3^+ on barium. The relative ratios H : H_2 : H^- per incident H_3^+ ion are found to be 1.80:0.48:0.24. The new contribution offered by the low work-function barium surface is the 0.24 H^-/H_3^+. The H_2^- intermediary state has effectively converted the low-lying $H_2(\nu'')$ population into an additional source of H^- and H.

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