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ABSTRACT

The H_2^+ ions from the volume of a hydrogen discharge will strike the discharge chamber walls with a kinetic energy equivalent to the plasma potential. A three-step process is described in which the H_2^+ ions are neutralized in a two-stage Auger process followed by a third stage wall relaxation collision, with the net result that the incident ions are converted to ground state molecules having a broad vibrational excitation spectrum. For kinetic energies ranging from a few electron volts up to twenty electron volts a substantial fraction, $\simeq 2/3$, of these ions will reflect as molecules, and of this population a fraction as large as twenty percent will have vibrational excitation $v'' \geq 6$. This large vibrational population will provide a contribution to the total excited level distribution that is comparable to the E-V process. Implications for negative ion generation in an optimized tandem configuration are discussed.

INTRODUCTION

In the first of our companion papers[1] presented at this Symposium we have discussed the negative ion formation by dissociative attachment[2] to vibrationally excited molecules in a high density hydrogen discharge. The vibrational excitation was presumed to be generated by high-energy electron collisions, the E-V process, in the first chamber of a tandem system. Associated with the ionization of the discharge by the high energy electrons is the formation of H_2^+ molecular ions whose equilibrium concentration in a high-power, high-density discharge is typically twenty to thirty percent of the total electron density.[3] RF source experience has further shown, however, that under certain conditions the H_2^+ concentration can be as large as 80 percent of the electron density.[4]

The discharge normally assumes a positive potential with respect to the confining discharge walls and whose value is some multiple of the electron temperature. For the high-density discharges of interest here the plasma potential will nominally be in the range from a few volts up to about 20 volts. The molecular ions in the discharge are accelerated across this potential and strike the wall with the equivalent kinetic energy causing the formation of both vibrationally excited molecules and the dissociation of the H_2^+ ions into free atoms. The vibrationally excited molecules generated in this way will be an additive contribution to the fore-mentioned E-V excitation, and will contribute to the subsequent formation of negative ions.

Although this vibrational excitation mechanism has been recognized previously, only a qualitative description of the process was possible due to the lack of quantitative data for the wall excitation and dissociation processes.[5,6] In the second of our papers presented at this Symposium,[7] the vibrational relaxation of the diatomic system in wall collisions has been studied in sufficient detail that a quantitative description of the contribution of H_2^+ to negative ion formation is now possible.

THE NEUTRALIZATION PROCESS

When the H_2^+ ion approaches to within 10Å of the discharge wall, Auger neutralization occurs producing a vibrationally excited, $H_2(v")$, molecule in the ground electronic state. The analogue for H_2^+ Auger neutralization is the neutralization of the He^+ ion in wall collisions, a process that has been studied extensively both theoretically[8] and experimentally.[9,10] The principal neutralization mechansim for He^+ ions is a two-step Auger process wherein an electron is first captured into the 2s-level of He at a distance of 5-10 Å from the surface. The metastable 2^3s helium atom formed in this first capture then continues to drift toward the surface. At a distance of approximately 3-5 Å from the surface, a second electron is captured directly into the He ground state orbital and the 2s electron that was initially captured is ejected from the atom. The helium atom, upon reaching the surface, is now in its ground electronic configuration.

Since the electronic orbital configurations of He^+ and H_2^+ are identical, we shall postulate that the neutralization of H_2^+ proceeds by a similar two-step process. We first take note of the fact that the energies of the electronic states of H_2 are displaced upwards an amount

$$+\frac{1}{4}\frac{e^2}{z} \quad , \tag{1}$$

as a consequence of the image forces acting on the electron. The distance is the separation of center-of-mass of the H_2^+ ion from the image plane. At close separation from the image plane the magnitude of the image shift is bounded,[11] and for purposes of discussion we shall take this upper bound to be 1.5 electron volts. The work function of most simple metals is 4.5 electron volts or more. As a consequence, only one of the excited electronic states of H_2, namely the first excited $^3\Sigma_u$ state, is accessible for Auger capture in the first step of the capture process.

The H_2^+ ions in the discharge are formed in a broad spectrum of vibrational levels with the majority population distributed over the lowest five levels.[12] As a consequence the H_2 ($^3\Sigma_u$) will in turn be formed over a rather broad range of internuclear separations, R_N, ranging from less than 0.5 Å to more than 1.2 Å. Because of the repulsive shape of the $^3\Sigma_u$ potential, the two nuclei of the excited molecule will begin to separate as the molecule continues to drift inwards toward the surface. After moving inward an amount 2-5 Å, second electron capture directly to the ground state occurs, ejecting the $^3\Sigma_u$ orbital electron. At this point however, the molecule has expanded in size (larger R_N) and the ground electronic state is formed in a high, v" > 8, level.

There is in fact an optimum "matching time," or "matching velocity" of the incident H_2^+ ion such that the initially formed H_2 ($^3\Sigma_u$) state will separate along R_N by an amount equal to ΔR, which is just the proper amount to form a high v" level when the second electron capture occurs. If Δz is the drift distance separating the two points of electron capture, v(2+) the velocity of the incoming H_2^+ ion, v the mean "rollout velocity" in the $H_2(^3\Sigma_u)$ configuration, the optimum "matching velocity" is given by

$$v(2+) = v\,\frac{\Delta z}{\Delta R} \quad . \tag{2}$$

Because the initial distribution in R will be rather broad and because the point of separation between the first and second electron capture is not sharply defined, the optimum v(2+) will have a rather broad range of values for high v" formation. Inspection of the H_2^+, $H_2(^3\Sigma_u)$ potentials indicates that the optimum formation of high, v" > 8, level formation will occur for incident H_2^+ energies ranging from a few electron volts up to twenty electron volts.

The H_2(v" > 8) formed in the two-step capture process continues to drift toward the wall eventually colliding with it. According to the results of our calculations discussed in Ref. 7, two processes predominate: vibrationally excited molecules, H_2(v"), rebound from the surface, now with a broad spectrum of vibrational levels, or, dissociation of the H_2 occurs. The fraction of incident molecules that survive the wall collisions as bound diatomic systems is denoted by f_1 and listed in Table I for several initial H_2^+ ion energies. Of interest for negative ion production is the fraction of f_1 that is formed with v" > 6. We denote this fraction by f_2; the fraction of incident H_2^+ that survive as H_2(v" ≥ 6) is then f_1f_2.

In order to evaluate the contribution of the three-step neutralization process we shall need to take some kind of average over levels v" since a relatively broad portion of the upper spectrum will be populated at the time of the second electron capture. In Table I is listed the fractions f_1, f_2 for incident levels v" = 2, 8, and 12, and for several incident H_2^+ ion energies.

TABLE I

E	v"	f_1	f_2	f_1f_2
1 eV	12	0.68	0.22	0.15
4 eV	2	0.68	0.21	0.14
	8	0.45	0.59	0.27
	12	0.66	0.33	0.22
10 eV	2	0.50	0.20	0.10
	12	0.50	0.40	0.20

IMPLICATIONS FOR NEGATIVE ION FORMATION

The production of negative ions in the tandem discharge is proportional to the population of $H_2(v" \geq 6)$ generated in the first chamber. In Ref. 1 we have identified the electron and gas densities for optimum negative ion formation. To examine the consequences of H_2^+ wall neutralization, we compare this rate of $H_2(v" \geq 6)$ formation with the E-V rate used in Ref. 1. The rate for H_2^+ neutralization is given by

$$0.25\ cnv\ (2+)\ f_1 f_2\ A/V \quad , \tag{3}$$

where c is the sheath factor taken equal to 0.60, v(2+) is the velocity of H_2^+ ions moving toward the sheath, $v(2+) = (kT/M)^{1/2}$, and n the electron density in the discharge. The ratio A/V is the surface to volume ratio and is equal to 3/R, where R is the system scale length. Here we have chosen the density of H_2^+ to be equal to one-fourth the electron density.

The rate for $H_2(v'' \geq 6)$ formation by the E-V process is

$$n(f)N_2 \sum_{v''=6}^{14} \sigma(E\text{-}V,\ v'')\ v \equiv n(f)N_2S \qquad (4)$$

Here, n(f) is the fast electron ($E > 30$ eV) density, N_2 the gas density, and S the sum of E-V rates.[13] The ratio of Eqs. 3 and 4 is then

$$12 \times 10^{14}\ f_1f_2/N_2R \quad , \qquad (5)$$

where we have taken $kT = 5$ eV, $S = 8 \times 10^{-9}$, and assumed the fast electron density contribution is one-tenth the total electron density. In Ref. 1 we found that the optimum value for N_2R ranged from 2 to 10×10^{14} molecules cm^{-2} as the wall recombination coefficient γ ranged from 0.1 to 1.0. Taking the product f_1f_2 to be 0.15, the ratio (5) is near unity for the lower gas densities. It follows that the wall recombination of H_2^+ to form $H_2(v'' \geq 6)$ can make an important contribution to the total vibrational excitation and negative ion yield, comparable to that of the E-V process for the lower gas pressures. If the H_2^+ concentration can be enhanced compared to the positive ion species, the wall recombination process may dominate.

THE H_2^- STATES

The two lowest H_2 states, $^2\Sigma_u$ and $^2\Sigma_g$, lie a few volts above the H_2 $^1\Sigma_g$ ground state for internuclear separations, R_N, near the potential minimum and intersect the $^1\Sigma_g$ state near $R_N = 2$. In the presence of the wall the image potential will lower the energy of the negative ion states an amount $- 1/4\ e^2/z$, and raise the $^1\Sigma_g^+$ state an amount $+ 1/4\ e^2/z$. If the H_2 $^1\Sigma_g$ state has been formed in the two-electron capture process discussed in the previous section, the question remains as to whether or not the H_2^- state can form by capture of an additional wall electron with subsequent direct dissociation to H^-. Again we shall assume the maximum image shifts, IM, amount to 1.5 eV.

At a nuclear separation R_N equal to one Å and for the maximum image potential the $^1\Sigma_g$ state will lie approximately one electron volt above the $^2\Sigma_u$ state but 3.5 volts below the $^2\Sigma_g$ state. An electron bound to the metal with an energy greater than or equal to a work function of $\phi = 4.5$ electron volts cannot make a transition to the higher lying $^2\Sigma_u$, $^2\Sigma_g$ states.

At larger separations the energy difference between the metal-bound electron and negative ion states is narrowed. Asymptotically the two negative ion states merge and differ from the molecular ground state by twice the image potential plus the H^- affinity, A, and, thus, by an amount equal to 3.0 + .75 = 3.75 eV, a difference still too small to overcome the image potential. In general H_2^- formation is energetically not allowed unless,

$$2IM + A > \phi_u \quad .$$

This condition can be achieved with composite alkali/transition-metal minimum-work-function surfaces but not with simple metal surfaces.

Finally, simultaneous electron capture of two electrons to form $H_2^-\ {}^2\Sigma_m$ directly from H_2^+ is energetically possible. The rate of double capture would be expected to be small compared to the single capture rate. To compete with the single capture the double capture must occur when the diatomic system is still at relatively small R_N. The H_2^- ions formed at small R_N are highly susceptible to electron shakeoff rather than passing through the dissociation mode. This double capture process would not be expected to be competitive with the process described in the section entitled: Implications For Negative Ion Formation.

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