MODELLING OF NON-EQUILIBRIUM HYDROGEN DISCHARGES

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INTRODUCTION

Measurements[1,2] of H^- and D^- concentrations in plasmas indicate that mechanisms involving intermediate excited states are required to explain the observed large magnitudes and functional dependencies. Processes which involve excited states or ions are the following:

a. Dissociative attachment of electrons from vibrationally excited states of hydrogen molecules:

$$e + H_2 \rightarrow (V) \rightarrow H_2^- \, ({}^2\Sigma_u^+) \rightarrow H(1S) + H^-$$

b. Dissociative attachment of electrons from electronically excited long-lived states of hydrogen molecules:

$$e + H_2 \, ({}^3\pi_u) \rightarrow H_2^- \, ({}^2\pi_u) \rightarrow H(2p) + H^- \quad ;$$

and

c. Dissociative recombination of H_3^+ :

$$e + H_3^+ \rightarrow H_3^* \rightarrow H_2^+ + H^-$$

In the low pressure positive column discharge process (a) will be most important because of its much lower energy threshold. Under conditions of beam-generated plasmas or of large fractional ionization processes (b) and (c) become more important.

We have performed a theoretical investigation of the electron kinetics in low pressure hydrogen discharges, with particular attention to the generation of negative ions in such plasmas. Recent results of experimental and theoretical[3] studies have shown that the dissociative attachment cross-sections for electron impact of molecular hydrogen are very strong functions of the initial vibrational state of the molecule. The existence of this comprehensive set of cross-sections, which establish the vibrational level and rotational level dependencies of dissociative attachment from the ground electronic state, permits the evaluation of the effect of non-equilibrium level populations on the production rate of H^- in discharges.

CALCULATIONS AND RESULTS

Using the cross-section data for momentum transfer and the multiple inelastic processes outlined in Table 1, and a numerical solution of the Boltzmann transport equation for electrons in the two-term approximation, the electron energy distribution function (EEDF) was calculated for a range of the parameter E/N. Here E is the electric field in volts/cm and N is the total number density (cm^{-3}) of the discharge species. This enables the evaluation of the rate coefficient for the various processes as functions of E/N. Results are shown in Figure 1 for assumed zero vibrational and rotational temperatures. Note that over most of the E/N range, the input energy is channeled mainly into vibrational excitation, V; dissociation, D, and electronic excitation, EX. The dissociative attachment process from the ground vibrational state absorbs a very minor fraction of the discharge energy. Vibrational excitation is the dominant energy loss in the E/N range of 10-50 Townsends. The dominant excitation channel is V=0 to V=1.

To examine the influence of vibrational excitation on the rate of dissociative attachment, the problem was initially uncoupled and a Boltzmann distribution in the vibrational states was assumed. The dissociative attachment was calculated as a function of E/N for a realistic range of vibrational temperatures. The results are shown in Figure 2. As anticipated, there is a significant increase (X50) in the rate of dissociative attachment for the higher vibrational temperatures. In addition, the location of the maximum of the dissociative attachment rate shifts to lower energies, reflecting the lower threshold for dissociative attachment from excited vibrational states.

When the discharge is switched on, plasma chemistry changes occur. These influence the EEDF and the excitation rates. Calculations have been made for different fractions of molecular and atomic hydrogen. Some results are shown in Figure 3, illustrating the EEDF's for (E/N)= 40 Townsends. For this case, if (E/N) were somehow held constant as dissociation occurs, the actual rate coefficient for vibrational pumping is increased so that the net rate (up to 50% dissociation) would not change markedly even though the number of molecules has decreased. Under most experimental conditions however, E is constant so that as dissociation proceeds, (E/N) decreases and the rate coefficients decrease accordingly. The influence of superelastic collisions on EEDF is measurable but it does not markedly change the dissociative attachment rate.

More important at higher gas pressures are collision processes involving heavy particles: molecule-molecule and molecule-atom. The primary energy transfers that occur are vibrational-vibrational (VV) and vibrational-translational (VT).

Formally, each vibrational state population will be governed by an equation:

$$\frac{dN_V}{dt} = \sum_{I,J,K} R^{K,I}_{J,V} N_J N_K - \sum_{I,J,K} R^{I,K}_{V,J} N_V N_I$$

where N_V is the concentration of molecules in state V, and the R's represent generalized rate coefficients for the population or depopulation of state V. This set of equations is commonly referred to as the Master Equation.

We have utilized the V-V and V-T rate coefficients from the theory of Schwartz, Slawsky and Hertzfeld[4] as modified by Keck and Carrier.[5] These results were fitted to the theoretical calculations or Billing and the experimental data of Ducing.[7] These heavy particle rate coefficients were supplemented by the electron impact rates for vibrational excitation and dissociative attachment and the Master Equation was integrated. Since the temporal evolution is governed by the transition probabilities, V-V and V-T, which range over many orders of magnitude, the resulting time constants for the coupled set of equations differ substantially in magnitude. Consequently, we have utilized the multi-step implicit stiffly stable scheme proposed by Gear.[8]

The rate of excitation, R_{IJ}, of the vibrational state J from vibrational state I and the rate of dissociative attachment are calculated self-consistently with the existing excited state densities by solving the collisional Boltzmann equation for the EEDF (differing substantially from a Maxwellian). The calculation is then repeated to account for changes in the molecular vibrational populations which, in turn modify the electron distribution and, consequently, the vibrational excitation and dissociative attachment rates. The procedure carried on until a steady state solution for the EEDF and the vibrational populations is found.

Results are presented in Figure 4, for an E/N = 40 Townsend, fractional ionization of 10^{-7}, and a translational temperature of 300°K. The vibrational distribution is presented in a semi-log plot as a function of the normalized vibrational energy. A Boltzmann distribution, characterized by a temperature T_V, would appear in this format as a straight line with slope of (De/KT_V). In this example, the vibrational temperature associated with the first two levels "$T_{V(1)}$" is approximately 2000°K. However, the actual vibrational distribution exhibits a significant departure from this straight line behavior. This departure can be understood by considering the relative magnitude of the V-V and V-T exchange rates. At low vibrational quantum numbers the Master Equation is dominated by V-V exchanges. In this regime, the vibrational distribution is given analytically by the Treanor distribution.

Note that the population in vibrational states V=5, 6, 7 exceeds the Boltzmann (at T_V = 2000°K) values by two orders of magnitude. This enhanced non-equilibrium population, encountered under conditions of strong vibrational excitation and low translational temperature, is caused by V-V exchanges.

Thus, anharmonic pumping, which leads to an enhancement in the population of the high lying vibrational states, produces a substantial increase in the rate constants for dissociative attachment, $k_{DA}(V)$, where

$$k_{DA}(V) = \frac{N_V}{N} <\sigma_V(v)\ v>$$

These rate constants, also shown in Figure 4, exhibit a maximum for (E_V/D_0)= 0.5. This corresponds to the vibrational level V=5. The contribution of this level alone to dissociative attachment exceeds that of the ground state by almost three orders of magnitude.

Having established how the vibrational kinetics couple into the dissociative attachment coefficient, we examine the dependence of this coefficient on the fractional ionization and gas temperature. Using the numerical solution of the Boltzmann equation for the electrons and the coupled vibrational kinetics solutions, the dissociative attachment rate was calculated for fractional ionization ranging from 10^{-8} to 10^{-6} at gas temperatures of 100°, 200°, and 300°K. The results for an E/N = 40 Townsend are presented in Figure 5. Consider first the results at 300°K. At this temperature, the effective dissociative attachment rate per electron exhibits a linear dependence on fractional ionization. Thus, the net rate of dissociative attachment is quadratic in electron density for the range of conditions indicated. The reduction of the gas temperature from 300°K to 200°K enhances the anharmonic pumping which results in an increased vibrational population in the "plateau" region and an extension of this region to higher vibrational quantum number. As a result, a significant increase in k_{DA} is obtained. However, a further reduction in the temperature to 100°K produces only a small additional increase. This saturation of the enhancement reflects the leveling off of the dissociative attachment cross-sections for vibrational levels $V>6$ and the increased influence of dissociative attachment losses on the vibrational distribution.

CONCLUSIONS

As a result of this analysis, we conclude that under appropriate discharge conditions, the rate of production of negative ions in a hydrogen plasma can be significantly enhanced. For a high pressure discharge operating at an E/N of 40 Townsend and a gas temperature of 200^{o}K, the effective rate constant is increased over three orders of magnitude. Since the negative ion production is dominanted by contributions from high lying vibrational states whose populations are determined by non-equilibrium pumping, it is important to determine self-consistently the state of vibrational excitation when analyzing the H_2 discharge. Even in a discharge at low pressure, if the wall deactivation of the vibrational levels is not 100% effective, one may anticipate increased dissociative attachment.

The calculations indicate that production will be significantly enhanced by vibrationally exciting the molecular hydrogen and maintaining low translational temperatures by environmental control or by gas dynamic expansion. In order to limit dissociation and its subsequent vibrational quenching, operation at low E/N values is necessary. It is suggested that this may be achieved by external ionization or operation in a mixture that includes an additive such as xenon or nitric oxide which is efficiently ionized.

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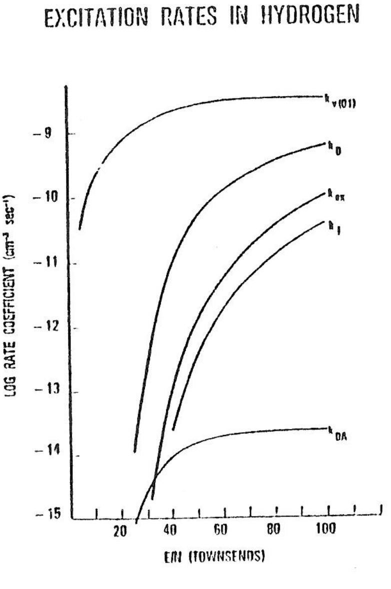

FIGURE 1. Excitation Rates In Molecular Hydrogen

$k_v(01)$ vibrational excitation V=0 to V=1.

k_D dissociations

k_{EX} electronic excitation

k_i ionization

k_{DA} dissociative attachment

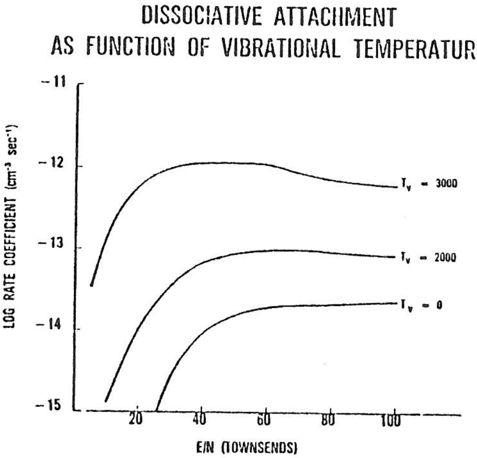

FIGURE 2
Dissociative Attachment in Hydrogen

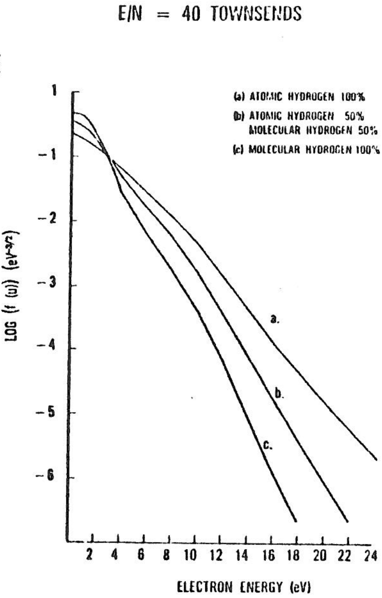

FIGURE 3
Electron Energy Distribution
in Atomic and Molecular
Hydrogen

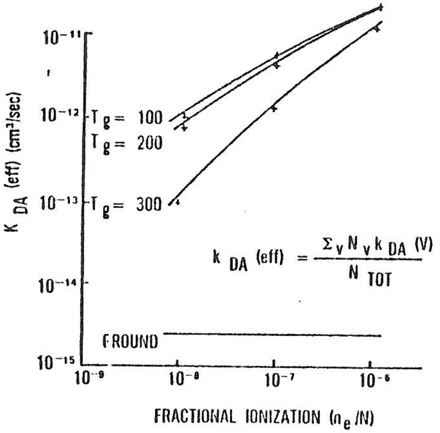

FIGURE 4
Non-Equilibrium Enhancement of
Dissociative Attachment

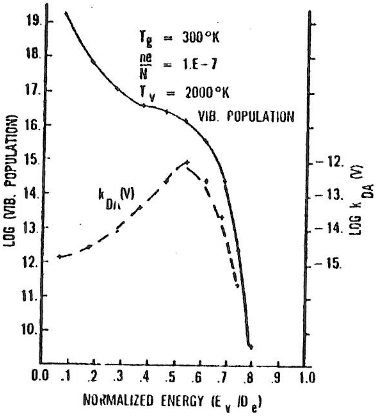

FIGURE 5
Self-Consistent Vibrational
Distribution and Rate of
Dissociative Attachment
in Hydrogen