KINETIC ANALYSIS OF EFFICIENT H^- FORMATION IN LASER IRRADIATED H_2

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ABSTRACT

It is shown that the rate coefficient of electron attachment to a species in laser irradiated H_2 is larger than that to $H_2(X^1\Sigma_g^+,\text{v})$ by up to 4 orders of magnitude. Kinetic analysis of the laser experiment suggests that possible precursors to H^- are the $E,F^1\Sigma_g^+$, and the high Rydberg states of H_2. The results show that the inclusion of this additional source term for H^- production may resolve some of the problems in understanding the H^- densities in low pressure H_2 discharges.

INTRODUCTION

The interest in the study of H^- formation stems from the need to generate intense neutral beams for fusion experiments [1], and for a variety of other applications. The most widely studied high density, low pressure H^- volume source in the literature is the multipole device where a magnetic filter is used to separate the plasma into two regions having fast and slow electrons [2, 3, 4]. The hot plasma region is used to generate the vibrational excited $H_2(X^1\Sigma_g^+,\text{v})$ and in the cold plasma region, H^- are thought to be efficiently produced by the following dissociative attachment (DA) processes.

$$e + H_2(X^1\Sigma_g^+, v) \xrightarrow{k_v^{DA}} H^- + H \tag{1}$$

The rate coefficients of process 1 are very strong functions of the initial vibrational state of the molecule [5].

Recently, very high formation efficiencies of H^- in laser irradiated H_2 have been reported [6]. It has been shown that electrons, produced through laser photoionization of H_2, attach very efficiently to a species formed by the same laser pulse to form H^-. However, the identity of the electron attaching species in the above experiments is ambiguous at least. This paper explores the possible identity of the attaching species through a kinetic analysis of the laser irradiation experiment reported in [6].

EFFICIENCY OF THE LASER IRRADIATION EXPERIMENT

In order to estimate the rate coefficient of electron attachment in the experiments of [6], consider the following excitation schematics.

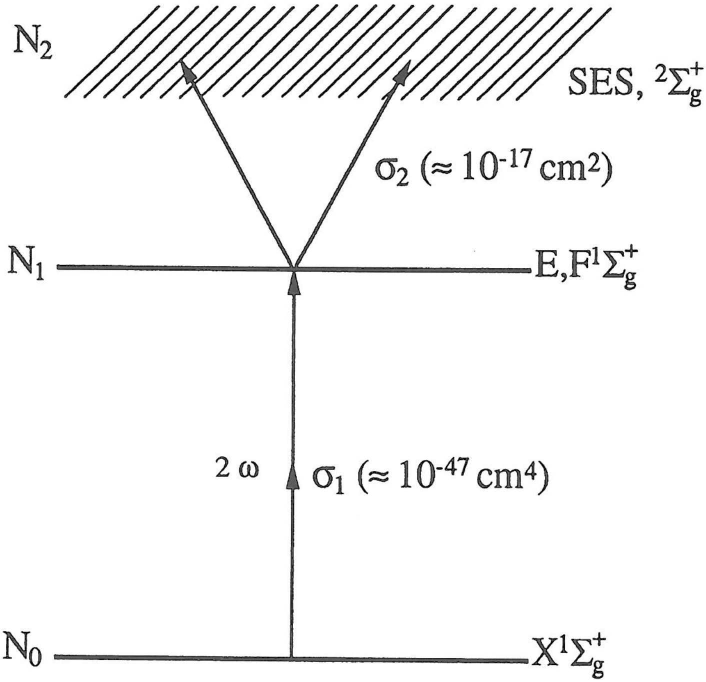

Figure 1: Schematics of the laser excitation experiment in H_2 [6].

Although the experiment is time dependent, as a first order approach, steady state is assumed in the analysis. The rate balance equations for the population densities of $H_2(E, F^1\Sigma_g^+)$ (N_1) and the super-excited states in the ionization continuum $(SES, (N_2))$ are then given by the following.

$$\frac{dN_1}{dt} = N_0\sigma_1 I^2 - N_1\sigma_2 I - k_r N_1 = 0 \quad (2)$$

$$\frac{dN_2}{dt} = N_1\sigma_2 I - k_{rs} N_2 = 0 \quad (3)$$

where I is the laser intensity, and k_r ($\approx 100\ ns$), k_{rs} ($\approx 10^{-14}\ s$) are the lifetimes of the $E, F^1\Sigma_g^+$, and SES respectively.

If it is assumed that DA occurs to $H_2(X^1\Sigma_g^+$,v) (if formed at 100% efficiency through $E, F^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$,v transitions), then a *lower* bound of the H^-

formation rate (k_a) can be obtained. For the experimental conditions of pressure (0.67 kPa, N_0=1.65 $\times$ 10^{17} cm^{-3}), and I = 2.9 $\times$ 10^{24} $cm^{-2}s^{-1}$, we get N_1 = 1.4 $\times$ 10^{11} cm^{-3} and N_2 = 4.0 $\times$ 10^4 cm^{-3}.

For a laser pulse of thickness d_L (0.7 cm), the voltage ratio (R_v) of the total signal V_T (electron + ions), to the signal of unattached electrons V_e is given by

$$R_v = \frac{V_T}{V_e} = \frac{\eta d_L}{1-\exp(-\eta d_L)} \approx \eta d_L \tag{4}$$

where η is the electron attachment coefficient. At the applied electric field E=25 V/cm, p=5 $torr$, the experimentally measured $R_v \approx 7.5$ [7]. The DA rate k_a is then given by

$$k_a = \frac{w_d \eta}{N_1} = \frac{w_d R_v}{N_1 d_L} = 1.7 \times 10^{-4}\ cm^3/s \tag{5}$$

where w_d = 2.3 $\times$ 10^6 cm^3/s (at E/N = 1.5 $\times$ 10^{-16} Vcm^2) is the electron drift velocity. Equation 5 suggests an attachment rate which is more efficient than that to $H_2(X^1\Sigma_g^+$,v) by $\approx$ 4 orders of magnitude. It has therefore been proposed that, laser irradiation, under some conditions can be more efficient than (1) in H^- formation [8].

The above analysis can now be used to discuss the possible precursor for H^- formation. We discuss four significant alternatives (also see [6]).

1. DA to the SES. The observed dependence of the negative ion signal with pressure in [6] indicates that collisionally enhanced electron attachment occurs in the interaction region. Since the lifetimes of the SES are very short ($\approx 10^{-15} - 10^{-14}s$), DA to the SES is quite unlikely.

2. DA to $H_2(X^1\Sigma_g^+$,v). This process is ruled out because the observed rates are orders of magnitudes faster than for optimistic populations and rates for these states in the literature [5].

3. DA to $H_2(E,F^1\Sigma_g^+)$. To our knowledge, DA to this electronic state has not been studied in the literature. The only available study is a calculation [9] for the $c^3\Pi_u$ state, which shows a relatively weak enhancement in the DA rate as compared to those of $H_2(X^1\Sigma_g^+$,v) with increasing v. Contrary to the analysis of [6, 8], efficient attachment to the $H_2(E,F^1\Sigma_g^+)$ cannot be ruled out.

4. DA to the highly excited Rydberg states (HR) of H_2which may be populated via the decay of the SES followed by collisional or radiative stabilization [6, 8].

Based on the above discussion, a plausible mechanism of efficient H^- formation in the laser irradiation experiment [6] is the following:

$$3h\nu + H_2 \quad \rightarrow \quad H_2^+ + e$$

$$
\begin{aligned}
2h\nu + H_2 &\rightarrow H_2(E,F^1\Sigma_g^+) \\
h\nu + H_2(E,F^1\Sigma_g^+) &\rightarrow H_2^{**}(SES) \\
H_2^{**}(SES) &\rightarrow H_2^R + h\nu \\
H_2(E,F^1\Sigma_g^+) + e &\stackrel{k^{DA}}{\rightarrow} H^- + H^R \\
H_2^R + e &\stackrel{k^{DA}}{\rightarrow} H^- + H^R
\end{aligned} \qquad (6)
$$

where H_2^R, and H^R are the high Rydberg states of H_2 and H atoms respectively.

H$^-$ FORMATION IN VOLUME SOURCES

We now discuss the implications of efficient DA in laser irradiated H_2 on the H^- formation in volume discharge sources. We refer to the recent work of [2] where detailed comparisons between the measured and calculated plasma parameters, H_2 vibrational spectra, and H^- densities in two multicusp volume sources have been reported. While the simulation results of [2] for the discharge parameters are in good agreement with the experimental data, there is an inconsistency between the experimental and calculated $H_2(X^1\Sigma_g^+$,v), H^- densities. The calculated densities of vibrationally excited states with $v \geq 5$ are higher than the measured densities. More importantly, the calculated H^- densities are lower than those measured by up to a factor of ≈ 4. A total discrepancy of a factor of ≈ 10 is implied. The inconsistency discussed above is not trivial due to the following reasons:

1. The simulation results of [2] (and most of the reported calculations such as in [10]) require enhanced populations in $H_2(X^1\Sigma_g^+$,v$\geq$5) for efficient H^- production through process 1. A branching ratio analysis reveals that up to $\approx 85\%$ of the H^- production from process 1 is from $H_2(X^1\Sigma_g^+, v \geq 5)$ [2].

2. The vibrational distributions of $H_2(X^1\Sigma_g^+$,v=0-8) in a H^- volume source have been measured using VUV spectroscopy [11]. Contrary to the requirements of the models for a "plateau" in $v \geq 5$, the measured distributions show a very distinct approximately linear falloff. These results suggest the need for additional processes leading to H^- formation in the simulations. The linear falloff in the population densities of $H_2(X^1\Sigma_g^+, v \geq 5)$ is also evident in *all* the measured data shown in [2]. It is obvious therefore that the requirements of the plateau in $H_2(X^1\Sigma_g^+$,v) in the models (to explain the experimental H^- densities) lead to an overestimation of the population densities for $v \geq 5$.

Some additional processes that have been suggested for resolving the above inconsistency are the effects of rotational excitation and, inclusion of spatial gradients in the vibrational spectrum [2, 11].

We have recently shown that the characteristic electron energy distribution in H^- volume sources leads to efficient excitation of the H_2^R states of H_2 [12].

A simple kinetic analysis of H^- generation in volume sources suggests that DA to these high Rydberg states of H_2 can be a comparable (or dominant) source term for H^- production [12]. Inclusion of this additional source term for H^- generation may thus resolve some of the above discussed discrepancies on H^- densities in low pressure H_2 discharges. We note that the energy dependencies for efficient generation of H_2^R and $H_2(X^1\Sigma_g^+, v \geq 5)$ in a H_2 discharge are the same (both require a high energy beam component in the electron energy distribution). However, the threshold energy for H_2^R excitation is ≈ 15 eV [13], whereas the E-V excitation of $H_2(X^1\Sigma_g^+, \mathrm{v} \geq 5)$ is efficient only at electron energies ≥ 20 eV [3]. Some experiments in volume sources have been reported at very low discharge voltages [14]. While the results of [14] cannot be taken as conclusive, it is encouraging to note that H^- are formed even at discharge voltages as low as 11 V.

It has been shown recently in the literature that there is a strong increase in H^- densities (by up to factors of 3-6) when the discharge in operated in pulsed mode [15]. The increase in H^- production in the post-discharge is attributed primarily to reduced detachement rates in the absence of fast electrons. In order to look for the additional H^- formation channels suggested by us, it is important to consider the characteristic time scales of the different processes in the post discharge period. Time resolved photodetachment measurements show that while the fast electron density decays in less than 1 μs in the post-discharge, there is a very rapid buildup of H^- densities, which peaks at ≈ 20 μs [15]. More importantly, the H^- current then decays with *two* different characteristic times scales of 100 μs and 200 μs respectively. However, the lifetimes of $H_2(X^1\Sigma_g^+, \mathrm{v})$ can be as long as ≈ 1 ms. The above results suggest the contributions of two different timescales towards the formation of H^- in the post discharge. It is interesting to note that the long lifetimes of H_2^R states (10-100 μs [16]) closely correspond to the first characteristic time scale of H^- densities in the post discharge.

It is to be noted that the series termination of the Rydberg states is strongly influenced by applied fields, and by the statistical microfield (Holtzmark field). If the high n states are also populated by recombination, then more will be accessible in the afterglow than in the active discharge. However, the field effect could be a serious limit on current density scaling of negative ion sources.

In conclusion, our work suggests additional contributions towards the formation of H^- ions in H_2 discharges which are comparable (or dominant) at least to the currently believed mechanism of dissociative attachment to $H_2(X^1\Sigma_g^+, \mathrm{v})$. The experimental data in the literature lends strong support (although not conclusive) to the existence of very efficient dissociative attachment from an excited electronic state or the high Rydberg states of H_2 in low pressure discharges.

ACKNOWLEDGEMENT

The work of R.N. has been supported by the Wright Laboratory.

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