Conf-921145--7

UCRL-JC-112220
PREPRINT

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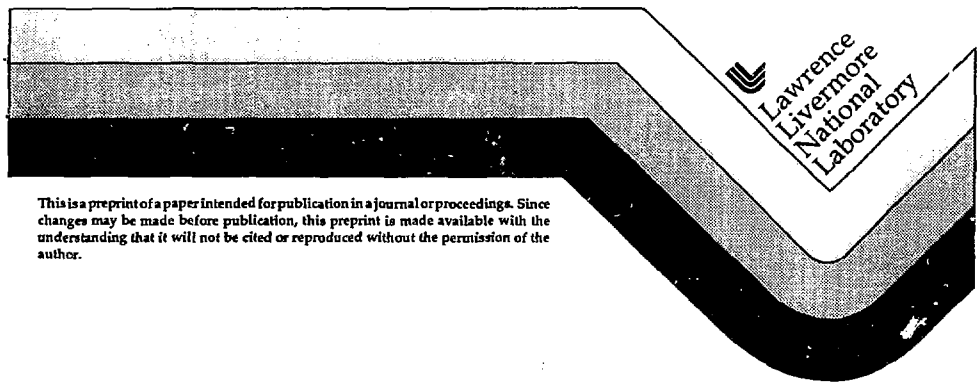
This paper was prepared for submittal to
American Institute of Physics Conference Ser. No. 000
6th International Symposium on the
Production and Neutralization of Negative Ions and Beams
Brookhaven National Laboratory, Upton Long Island, NY
November 9 -13, 1992

November 6, 1992



ATOMIC PROCESSES IN HYDROGEN AND DEUTERIUM NEGATIVE ION DISCHARGES

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INTRODUCTION

A knowledge of the atomic processes active in a hydrogen negative ion discharge and their respective rates is an essential component of the interpretation, modeling, and enhancement of negative ion systems. The generation of the cross sections and rate processes appropriate to this problem has been a principal activity at several laboratories[1-5]. In this paper is discussed those collision processes that are of major importance for the destruction of the vibrationally excited molecules generated in the discharge, processes that are essential to the valuation of the optimization procedure that is to be discussed in the following paper.

The negative hydrogen discharge was modeled first by Dubarry and Gautherin[6], who took into account H^- formation by dissociative attachment and polar dissociation of ground state molecules ($\upsilon = o$) in equilibrium with associative detachment and collisional detachment collisions,

$$e + H_2 \rightarrow H^- + H, \quad \text{(DA and PD)} \tag{1}$$

$$H^- + H \rightarrow H_2 + e, \tag{2}$$

$$e + H^- \rightarrow 2e + H. \tag{3}$$

The description of this problem is given by a single first-order differential equation and the solution of this equation is easily accessible.

Following the demonstration by Alan and Wong[7] that dissociative attachment proceeds successively more rapidly as the vibrational excitation increases through the $\upsilon = 4$ excited vibrational level, dissociative attachment theory was extended to the upper portion of the spectrum by Wadehra and Bardsley[8] employing a dissociative attachment model developed earlier by Bardslery et al.[9]. Upon fitting the calculated cross sections at one experimental value, the theory provided a basis for extrapolation over the full vibrational spectrum. The considerable sensitivity of these cross sections to the level of vibrational excitation that was indicated by both the theory and experiment necessitated that all vibrational levels be included in modeling the dissociative attachment (DA) process.

The e-V[10, 11] and E-V[5] electron excitation processes that generate the spectrum of vibrational population are themselves a function of vibrational level, but less sensitively dependent than is DA. A full-spectrum model for H^- generation includes, then, a set of fourteen coupled linear differential equations to define the excited vibrational population distribution, an additional set of fifteen rate equations to give the DA H^- yield per vibrational level, and a single final equation summing the individual contributions to give the total H^- concentration.

The solution of this full-spectrum model[12] served to make explicit those portions of the vibrational spectrum that were sensitive to the e-V process, and those portion sensitive to the E-V process. The full-spectrum model was subsequently applied to the analysis of medium-density hydrogen discharges[13].

In 1985, the Bari time-dependent gas-kinetics code[14] was extended to include the E-V and DA processes, and this expanded version has come to be employed by the groups at Bari[15] and at the Ecole Polytechnique[16] for the analysis of single-chamber multi-cusp discharges. A feature of these solutions[15] is the explicit display of the time variation of the atomic concentration and the vibrational population concentration. The development of these models has progressed as more accurate information of the atomic rate processes has accrued. More recently, independent development of the full-spectrum model has been progressing at Yamaguchi[17] and Keio Universities[18].

VIBRATIONAL DESTRUCTION PROCESSES AND CROSS SECTIONS

The principal sources of destruction of the vibrational level populations, in the order of their importance, are as follows:

$$e + H_2(\upsilon) \rightarrow e' + H_2(b^3\Sigma_u^+) \rightarrow e' + H + H, \tag{4}$$

$$e + H_2(\upsilon) \rightarrow e' + H_2^*, \tag{5}$$

where H_2^* includes all singlet excitations and triplet excitations above the $b^3\Sigma_u^+$ state,

$$H + H_2(\upsilon) \rightarrow H + H_2(\upsilon' < \upsilon), \tag{6}$$

and the V-T process

$$H_2 + H_2(\upsilon) \rightarrow H_2 + H_2(\upsilon' < \upsilon). \tag{7}$$

The dissociation reaction, (4), is driven mainly by the thermal electron component present in the discharge. For $\upsilon = o$ this reaction has been studied extensively both experimentally[19,20] and theoretically[21-23], the quantal calculations displaying a close fit in the range of available experimental data, 10-30 eV. For $o < \upsilon \leq 9$ classical Gryzinski-type calculations have been performed by Cacciatore et al.[24], and quantal calculations by Rescigno and Schneider (RS)[25] for incident electron energizer E > 12 eV. For $\upsilon = o$ the classical results reproduce the cross section maximum, but fall well below the experimental values at lower energies. Since the application here is to thermal discharges in the range 3-5 electron volts, the higher υ classical cross sections may be suspect in the relevant low-energy range. While quantal calculations for higher υ and low energies do not exist, the shortfall of the classical values at the lower energies has deemed it worthwhile to interpolate-extrapolate the RS cross sections to threshold.

An upper limit to the dissociation cross sections at large υ can be obtained by taking note that the process (4) is essentially an electron spin-exchange reaction[25], and at large internuclear separations, appropriate to large υ, the molecular collision tends to an atomic collision. When viewed as a spin-exchange collision we can write the dissociation collision as

$$e(\uparrow) + H_2(\upsilon, \uparrow\downarrow) \rightarrow e'(\downarrow) + H_2(b^3\Sigma_u^+ \uparrow\uparrow) \rightarrow e'(\downarrow) + H(\uparrow) + H(\uparrow). \tag{8}$$

The incoming electron exchanges with a bound electron of opposite spin to form the $b^3\Sigma_u^+$ dissociating state.

The cross section for electron spin-exchange by electrons incident upon atomic hydrogen has been evaluated by Temkin and Lamkin[26,27] and by Dalgarno and Rudge[28]. For a statistical mix of para and orthohydrogen, the equivalent cross section for $H_2(\upsilon)$ at large υ tends to

$$\sigma = \frac{3}{4}\frac{\pi}{k^2}\sum_{\ell=0}^{2}(2\ell+1)\sin^2(\eta_{\ell^+} - \eta_{\ell^-}). \tag{9}$$

Interpolation – extrapolation of the dissociation cross sections

$$\sigma(E) = \frac{1}{E} \int T_{\ell m \ell' m'}^{2} \, dR$$

Rescigno and Schneider

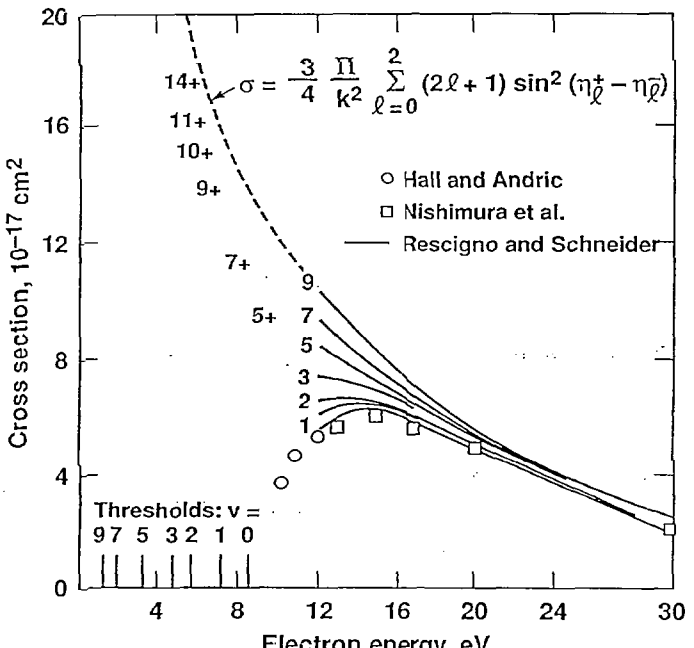

Fig. 1

The η_{ℓ^+} and η_{ℓ^-} are the spin zero and spin one phase shifts, respectively. This cross section is shown in Fig. 1, joining with the RS cross section for $\upsilon = 9$ at the higher energies. Also shown in Fig. 1 is the position of the different level thresholds as defined by the outer turning points. For the lower υ levels, those RS cross sections that extend to low enough energy to exhibit a cross section maximum the energy interval between threshold and maximum is seen to be approximately constant. Carrying this observation to the higher levels, the maxima positions for these higher levels is given by the vertical component of the crosses. In Ref. 25 the RS cross sections are given as the product of the coefficient E^{-1} and an integral function over the internuclear separation. Inspection of the RS data shows the integrand to be approximately constant near the cross section maxima; the successive higher υ maxima are then scaled as E^{-1}, shown by the horizontal bar portion of the crosses. The similar curvature of each of the lower cross sections vesus energy near their maximum reflects in part the identity of initial and final electronic states in all cases; this curvature is transposed to the higher υ levels and the cross sections interpolated linearly to threshold. The resulting interpolated cross sections are shown in Fig. 2. Inspection of the figure shows the cross sections to be substantially larger than those of Cacciatore et al.[24] for incident electron energies below the respective maxima.

The principal loss of H_2 (υ) by high energy electrons are the electronic excitation reactions (5). The leading excitations are to the $B^1\Sigma_u^+$ and $C\ ^1\Pi_u$ states. A comparison of the relative cross sections calculated by the Bari[24] and Livermore[5] groups is shown in Fig. 3. The disparities are large starting immediately above the ground vibrational level.

The V-T rates for H_2 and HD have been recalculated recently by Cacciatore et al.[3] using a new semi-classical collision model developed by Cacciatore and Billing.[2] The H_2 rates for a gas temperature of 500°K are compared in Fig. 4 to earlier values used by Hiskes and Karo (HK).[29] In both sets of data the lowest υ rates are set by the experimental data, while the extrapolation to higher levels is based upon theoretical arguments or models. The HK rates for the highest vibrational levels were linked to the H-H elastic scattering cross section. The new Cacciatore results are based upon an improved interaction potential, and utilizing a large number of molecular trajectory calculations. These new rates are adopted here.

Finally, we comment on the atom - H_2 (υ) vibrational relaxation cross sections, reaction (7). In Fig. 5 the recent values of Lagana[4] are compared with earlier values employed by HK[29], values that were derived from an extensive number

Dissociation cross sections

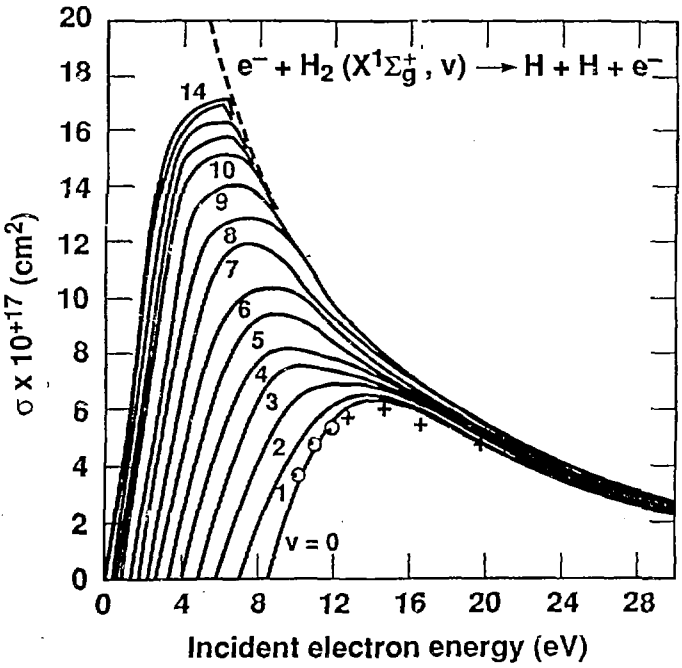

Fig. 2

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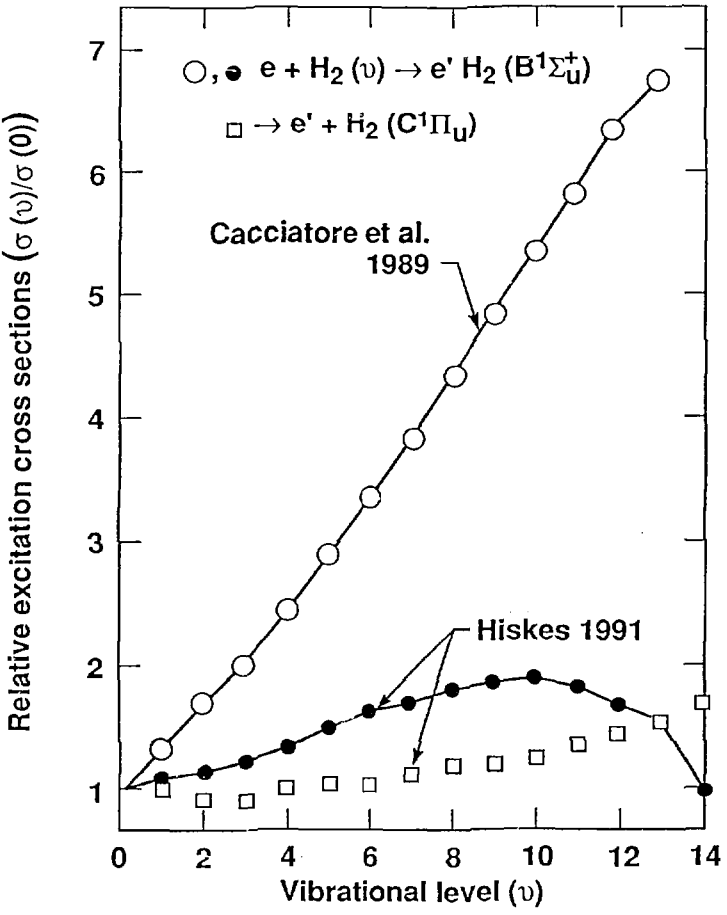

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Fig. 3

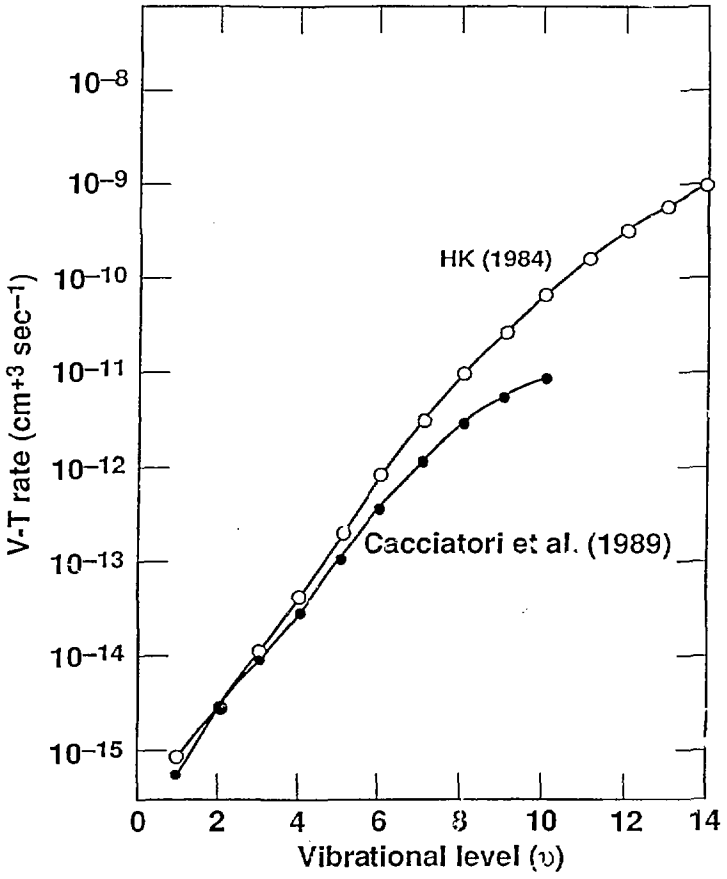

Fig. 4

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of molecular trajectory calculations performed by Blais and Truhlar (BT)[30]. The Lagana trajectory analysis and model is similar to that of BT. While the Lagana rates are as much as a factor of two larger for certain levels, υ, than those rates employed earlier, the uncertainty in the atomic concentration in the discharges that are under study is at least as great as the differences in these two sets of rates.

In summary, the new cross section values and rates discussed here differ substantially from previous values used in hydrogen discharge analysis, and these new rates will impact on current modeling studies. These new rate values are employed in the two following papers presented at this conference.

ACKNOWLEDGEMENT

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Fig 5

Atom-molecule vibrational relaxation

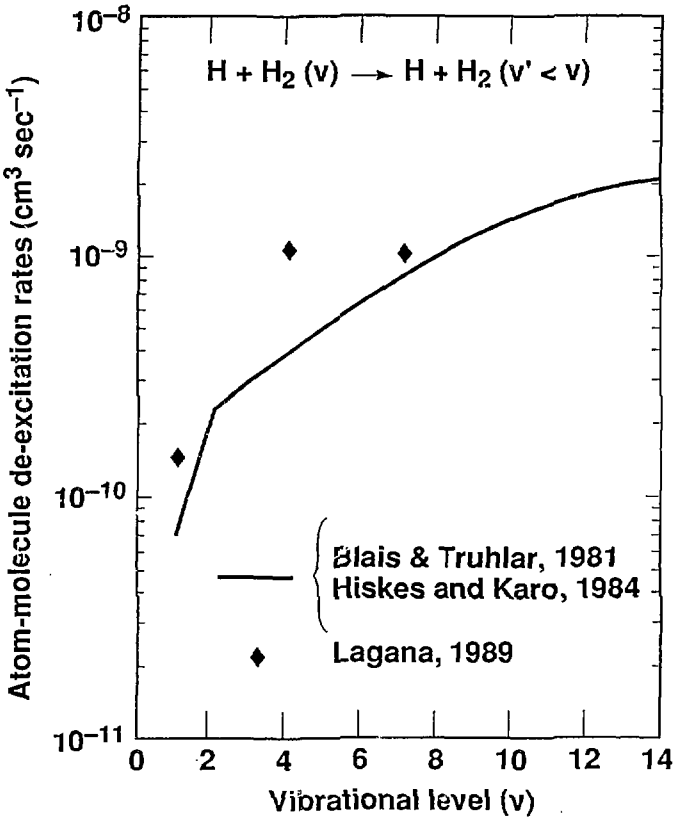

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Fig. 5

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