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MASTER

BY

D. H. MCNEILL

**PLASMA PHYSICS
LABORATORY**

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**PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY**

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DISSOCIATIVE EXCITATION AS THE SOURCE OF
NEUTRAL ATOMS IN HYDROGEN DISCHARGES

D. H. McNeill

ABSTRACT

Electron impact dissociative excitation of H_2 molecules is identified as the origin of the narrow width and structure of Balmer lines observed in various low density hydrogen discharges. On the basis of this data and estimates of the rates of competing processes in plasmas, dissociative excitation, together with other molecular reactions, is proposed as the source of neutral atoms and protons in these discharges.

The manner in which hydrogen atoms enter a discharge is of fundamental importance in basic discharge physics and fusion research. The low energy neutral atoms observed spectroscopically in hydrogen discharges are often assumed to have undergone wall recycling (as atoms) and energy degradation. In certain discharges the Balmer alpha and beta lines always have half widths of less than $0.5 \text{ \AA}$ that vary little with the discharge and plasma parameters. The shape of the profile in the wings, however, does vary with the electron temperature. Here I offer dissociative excitation of gaseous phase molecular hydrogen as an explanation for the narrow width and structure of the Balmer lines and (together with similar reactions of H_2^+ ions) as a source of the "fresh" neutral atoms and protons in these discharges. This explanation is consistent with data on the H_α spectrum from ion sources for neutral beam injectors and from the Elmo Bumpy Torus and may help solve numerous problems in the physics of these other discharges. A brief discussion is given of the processes by which H atoms and H^+ ions are produced in the plasma volume. While more detailed analysis is clearly needed, the role of dissociative excitation in the production of protons and atoms in these plasmas is supported by rough estimates of the volume rates for various relevant processes as well as by the spectroscopic data.

Electrons striking a neutral hydrogen molecule may cause several reactions. The principal reactions of this type are listed in Table 1 with their electron onset energies. The most important of these reactions are molecular dissociation (referred

to as dissociative excitation if a product atom is excited -- the terms are often used interchangeably) and molecular ionization. The product H atoms from reactions (1) and (3) and from electron impact dissociation of the H_2^+ ions formed in reaction (2) may be excited and it is these which are observed spectroscopically. The two onset energies given for molecular dissociation correspond to the measured onset energies for molecular dissociation (without excitation) [1] and for dissociative excitation to the $H(n)$ state ($n \geq 2$) [2,3], respectively. The onset energy given for reaction (3) is for an unexcited product atom and excitation may occur at higher electron energies. The cross sections for reactions (1), (2), and (3) are plotted as functions of the electron energy in Fig. 1 [1,4,5]. (The cross section for reaction (4) with cold H_2 is negligibly small on this scale.) Protons are formed in further reactions with the products of reactions (1) and (2). In particular, electron impact dissociative excitation and dissociative recombination of the molecular ion formed in reaction (2) have very large cross sections so reaction (2) may be followed quickly by the formation of protons and neutral atoms. Reaction (1) is followed by electron ionization or by charge exchange of the atoms to yield protons.

Dissociative excitation yields H atoms in two energy groups (first measured in 1967 by Leventhal, Robiscoe, and Lea) [2]: slow (atom energies $E \sim 0.3$ eV for electron energies $E_e \geq 15-18$ eV) and fast ($E \sim 2-8$ eV for $E_e \geq 28$ eV; the customary Franck-Condon energy). These energy groups have been examined in electron beam experiments by both time-of-flight and spectroscopic techniques. Figure 2 shows some experimental energy spectra of

fast and slow H(2s) atoms produced by dissociative excitation of H₂ molecules (solid curves) [3] compared with Maxwellian energy distributions having the same most probable energies (dashed curves). The data of Fig. 2(a) and (b) were taken for E_e=80 eV and 40 eV, respectively, and in both cases the metastable H(2s) atoms were detected at an angle of 80° to the electron beam. The peaks of the energy distributions of the product atoms shift slightly to higher energies as E_e is increased [3]. Both fast and slow dissociation products have been observed during bombardment of H₂ gas with electrons at energies of up to 1000 eV (dissociative ionization, in practice a special case of dissociative ionization, dominates for E_e ≥ 60 eV). Other reactions (including dissociation of H₂⁺, dissociative ionization of H₂, and photoionization of H₂; besides dissociative excitation of H₂ have been found experimentally to yield atoms or protons in the 2-12 eV energy range, although, to the best of my knowledge, the slow group has not been looked for except in the case of dissociative excitation and dissociative ionization of H₂. Thus, several processes may contribute to (at least) the fast atom component observed in plasmas. Figure 3 shows the kinetic energy spectra of the fast products in four cases [3,6,7]. The bulk of these energy spectra lie in the range 2-8 eV. (Since the rate of dissociative ionization of H₂ is small compared with competing proton-producing processes, the contribution of, for example, curve 4 of Fig. 3 to the overall atom energy distribution in plasmas will be relatively small.)

The existence of these two groups of dissociation products explains well the spectroscopic observations which I shall now discuss. The measurements were made on the Elmo Bumpy Torus (EBT) and on neutral beam injector ion sources. EBT is a steady state microwave-heated (up to 60 kW in the experiments reported here) toroidal device with a major radius of 150 cm and a minor radius of 25 cm (at the observation point) [8]. The ion sources are low-density pulsed (≤ 200 msec) arcs with dimensions on the order of 25 cm [9]. Table 2 illustrates some of the cases examined on these devices and lists the discharge conditions and H_{α} spectrum data for each. Raw data from Fabry-Perot interferometer traces obtained in each of the regimes listed in this table are plotted in Fig. 4. From the bottom to the top of Fig. 4 there is a rough progression from low to high electron temperatures. The widths of the fast (where it exists) and, especially, the slow components appear to be invariant under all conditions. In the EBT data the ratio of the areas of the slow and fast (where it exists) components ranges roughly from 1 to 3 when the fill pressure and other conditions are varied (the fast component may be absent at pressures corresponding to the transitions between modes, as it is at high pressures). The energies associated with these Doppler widths correspond to the energies of the product atoms found in dissociative excitation of the hydrogen molecule [2,3], and no narrower spectral component (as is seen in much smaller and colder discharges) which might correspond to the wall temperatures is found in these data.

In the dense fill microwave discharge on EBT (case F) there is no fast (wide) H_α component (down to less than 2% of the peak intensity). This is an indication of a low electron temperature. For example, in a plasma with an electron temperature $T_e = 4$ eV, 3% of the electrons have $E_e \geq 18$ eV and are able to participate in dissociative excitation to yield the $n=3$ state of hydrogen, and of these (the 3%), 9% have $E_e \geq 28.5$ eV and are capable of producing the fast dissociation component. Thus, for $T_e = 4$ eV, roughly 4.5% of the excited product atoms belong to the fast group (assuming that half of the atoms produced by electrons with energies above 28.5 eV are in each group). The H_α emission is most intense in this case (F) and, as many low temperature microwave discharges are, the plasma is evidently a rich source of H atoms. The ion source discharges (cases E and D; also with low temperatures [9]) also have only a slow component. [A slow atom energy spectrum of the form given in Fig. 2(a) yields an H_α spectrum of the form shown in Fig. 4 (d, e, and f) when the instrument profile (Airy function) of the interferometer is included.] The other, lower pressure operating regimes of EBT (the T mode, our case A, is the typical operating regime of this device) have significantly higher electron temperatures (measured by Thomson scattering) and both groups of atoms show up in the spectrum. [The straight line fits in curves a, b, and c of Fig. 4 do not necessarily indicate a thermal energy distribution of the fast component for $\Delta\lambda^2 \leq 0.2 \text{ \AA}^2$, as a fast component energy distribution with a low energy cutoff, as in Fig. 2(b), will have a flat spectral distribution for $\Delta\lambda$ smaller than the Doppler shift

corresponding to the cutoff.] Thus, as the electron temperature goes above a few eV, a fast atom component appears, while at low T_e only the slow component is observed.

At low T_e nearly all the atoms (and protons) in the discharge should be due to molecular dissociation [reaction (1)] which yields protons upon ionization of the product atoms, rather than to molecular ionization [reaction (2)] which is followed by further electron impact reactions to produce both atoms and protons. For example, when $T_e = 2$ eV the rates for reactions (1) and (2) are 3×10^{-10} and $\sim 6 \times 10^{-12}$ cm^3/sec , respectively, while when $T_e = 4$ eV the corresponding rates are 3×10^{-9} and 4×10^{-10} cm^3/sec . The rates for these two reactions are equal ($\sim 1 \times 10^{-8}$ cm^3/sec) when $T_e = 12$ eV, after which reaction (2) proceeds more rapidly. Whether reaction (1) alone or reaction (2) followed by other processes is the origin of most of the H atoms in a discharge thus depends primarily on the plasma electron temperature. Which of these two reactions is the dominant source of protons in the volume of a plasma is also determined by the mean free path for the succeeding proton-producing reactions (i.e., by the electron density as well as by the electron temperature) and by the plasma volume. In general, for a given electron density, the larger the plasma volume is, the lower the temperature above which the chain starting with reaction (2) becomes the dominant source of protons. In a very small (≤ 1 cm), cold discharge, wall reflections of H atoms produced by molecular dissociation will become important as a source of excited atoms and protons in the discharge (even if the reflection coefficient for atoms is small) as is indicated by the much narrower H_α linewidth seen

in low density discharges of this type, apparently as a consequence of equilibration with the vessel walls.

Assuming a uniform distribution of the electron density and temperature and of the molecular density in the discharges of cases D, E, and F, it can be shown that the rate of H_α production by dissociative excitation is at least comparable to the observed average volume emissivity from these plasmas. A more complete analysis, including the variations in the plasma parameters across the discharge chamber is obviously needed for these and the other cases. However, the facts that the observed intensity and line shape can be explained in terms of the reaction rate and product energy spectrum of dissociative excitation and that there is no energy component in the H_α spectra which corresponds to reasonable values of the wall temperature support the idea that volume processes involving H_2 molecules which enter the discharge as feed gas or from the walls (as molecules, not atoms) are responsible for the atoms and ions in the discharge.

At the dissociation energies (about 0.3 and 3 eV), product atoms in the $n=2(p)$, 3, and 4 states will emit photons over a mean free path of less than 1 cm so they will be observed near where they are produced. In the plasmas discussed here, the mean free path for ionization of the atoms (slow or fast) produced by dissociative excitation is comparable to or greater than the plasma dimensions. Thus, the neutral density profile must be fairly uniform. In much hotter and denser plasmas such atoms will exist only near the edge and a much faster charge-change neutral component may produce significantly larger Doppler widths than seen in this data. The slight difference between the

widths of the slow component for the ion sources and for the EBT discharges is due to Zeeman splitting in the 2-5 kG magnetic field in the viewing volume of EBT. This suggests that some of the hydrogen Balmer line profiles obtained from hotter, denser, and higher-magnetic-field plasmas can be interpreted in terms of these dissociation components and the Stark or Zeeman broadening of their line emission.

I made these measurements of H_α profiles on the neutral beam injector ion sources and EBT some years ago at ORNL. The observed narrow linewidths can now be explained consistently. Evidence for the occurrence of dissociative excitation of H_2 includes the appearance of neutral atoms with energies of about 0.3 eV over all the observed discharge regimes (fill pressure, magnetic field, electron temperature, wall conditions, heating mechanism, etc.), the existence of large amounts of neutral hydrogen molecules in the discharges (H_2 line spectrum), and the appearance of a fast neutral atom component with an energy of about 3 eV at higher electron temperatures. Furthermore, based on rough estimates of the rates of the processes involved, these discharges are large enough to ensure that volume effects dominate. Thus, in these plasmas, gas molecules, rather than the walls, as commonly assumed, appear to be the source of "fresh" neutral atoms and protons. This conclusion requires further testing based on model solutions of the rate equations for plasmas under various wall and volume source conditions. This and related work are in progress.

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TABLE CAPTIONS

Table 1. The principal reactions of hydrogen molecules with electrons.

Table 2. A listing of the observed discharge conditions and the corresponding H_{α} profile characteristics.

TABLE 1

Reactions of Hydrogen Molecules with Electrons

<u>Reaction</u>	<u>Name</u>	<u>Onset Energy</u>
1. $e + H_2 \rightarrow H + H + e$	Molecular dissociation (Dissociative excitation)	8.8 eV (15-18 eV)
2. $e + H_2 \rightarrow H_2^+ + 2e$	Molecular ionization	15.4 eV
3. $e + H_2 \rightarrow H^+ + H + 2e$	Dissociative ionization	18 eV
4. $e + H_2 \rightarrow H + H^-$	Dissociative attachment	<1 eV

TABLE 2

<u>Case</u>	<u>Discharge and Conditions</u>	<u>Width* of H Alpha Profile($\text{\AA}$)</u>		
		<u>Apparent Total</u>	<u>Slow Component</u>	<u>Fast Component</u>
F.	EBT dense fill C mode, diffuse (fill pressure $\sim 4 \times 10^{-5}$ Torr gauge); $\bar{n}_e \sim 6 \times 10^{11} \text{ cm}^{-3}$; T_e low.	~ 0.3	~ 0.3	none
E.	7 cm duopigatron source; $\bar{n}_e \sim 2 \times 10^{12} \text{ cm}^{-3}$; $T_e = 2-4 \text{ eV}$.	0.25 ± 0.03	0.25	none
D.	10 cm modified MacKenzie source; parameters as in Case E.	0.26 ± 0.04	0.26	none
C.	EBT medium fill C mode, diffuse (1.8×10^{-5} Torr gauge); $\bar{n}_e \sim 6 \times 10^{11} \text{ cm}^{-3}$; $T_e \sim 20 \text{ eV}$.	0.39 ± 0.05	0.27	0.82 ± 0.15
B.	EBT low pressure M mode, diffuse ($3-4 \times 10^{-6}$ Torr gauge); $\bar{n}_e \sim 3 \times 10^{11} \text{ cm}^{-3}$; T_e unknown.	0.38 ± 0.05	> 0.25	0.70 ± 0.20
A.	EBT typical optimum operating T mode (6×10^{-6} Torr gauge); $\bar{n}_e \sim 4 \times 10^{11} \text{ cm}^{-3}$; $T_e \sim 120 \text{ eV}$ (at center).	0.38 ± 0.02	0.27	0.90 ± 0.07

*Instrument width and H_α fine structure (modelled as two equal peaks separated by $0.14 \text{ \AA}$) deducted.

Fig. 1. The cross sections for electron impact (1) molecular dissociation [1], (2) molecular ionization [4], and (3) dissociative ionization [5] of H_2 as functions of the electron energy.

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Fig. 2. Experimental time-of-flight measurements of the kinetic energy distributions of slow (a) and fast (b) H(2s) dissociative excitation products (solid curves) [3] compared with Maxwellian energy distributions having the same most probable energies (dashed curves).

Fig. 3. The kinetic energy distributions of the fast ⁷⁹⁺³²⁴ component product particles from various electron impact molecular processes: (1) H(2s) from dissociative excitation of H₂ by 40 eV electrons, detection at 80° to electron beam direction [3]; (2) same, with 70 eV electrons [3]; (3) calculated energy of dissociation products from impact of electrons with $E_e \gg 25$ eV on H₂⁺ ions [6]; and (4) protons from dissociative ionization of H₂ by 300 eV electrons [7].

Fig. 4. Raw data from Fabry-Perot interferometer traces of the H_{α} emission from the plasmas listed in Table 2 (relative signal versus the square of the wavelength shift $\Delta\lambda$ from the peak intensity point).

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