TOPICAL REVIEW

Collisional kinetics of non-uniform electric field, low-pressure, direct-current discharges in H₂

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Abstract

A model of the collisional kinetics of energetic hydrogen atoms, molecules and ions in pure H₂ discharges is used to predict Hα emission profiles and spatial distributions of emission from the cathode regions of low-pressure, weakly ionized discharges for comparison with a wide variety of experiments. Positive and negative ion-energy distributions are also predicted. The model developed for spatially uniform electric fields and current densities less than 10⁻³ Am⁻² is extended to non-uniform electric fields, current densities of 10³ Am⁻² and electric field to gas density ratios E/N = 1.3 MTd at 0.002–5 Torr pressure. (1 Td = 10⁻²¹ V m² and 1 Torr = 133 Pa.) The observed far-wing Doppler broadening and spatial distribution of the Hα emission is consistent with reactions among H⁺, H₂⁺, H₃⁺ and H⁻ ions, fast H atoms and fast H₂ molecules, and with reflection, excitation and attachment to fast H atoms at surfaces. The Hα excitation and H⁻ formation occur principally by collisions of fast H, fast H₂ and H⁺ with H₂. Simplifications include using a one-dimensional geometry, a multi-beam transport model, and the average cathode-fall electric field. The Hα emission is linear with current density over eight orders of magnitude. The calculated ion-energy distributions agree satisfactorily with experiment for H₂⁺ and H₃⁺, but are only in qualitative agreement for H⁺ and H⁻. The experiments successfully modeled range from short-gap, parallel-plane glow discharges to beam-like, electrostatic-confinement discharges.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The objective of this review is to test the ability of a previously developed model [1] of the kinetics of energetic ions, atoms and molecules in low-current discharges to explain quantitatively experimental observations of Hα emission and ion-energy distributions from the cathode regions of a wide variety of low-pressure, moderate-current discharges in pure hydrogen. In particular, calculated Hα Doppler-broadened profiles, spatial distributions of spectrally integrated emission and relative mass-identified ion flux energy distributions are reviewed and compared with experiment. The ability of the model to predict the observed emission in the far wings of the Hα profile is tested over wide ranges of current density and electric field to gas density E/N. The model utilizes cross-sections and reaction pathways for various species in the production of fast H(n = 3) atoms established for uniform electric fields in [1–3]. The model is extended to approximately describe the highly non-equilibrium behavior of the electrons in the spatially varying...
electric fields of the cathode fall and the negative glow. The production, transport and $H_n$ excitation by negative ions are estimated. The present steady-state model does not include radiofrequency discharges, although many features of the observed $H_n$ emission and the model are common to dc and rf discharges.

The observation of ‘excess broadening’ in the wings of the $H_n$ lines emitted by dc glow discharges in $H_2$ began many years ago. Sternberg and coworkers [4] found asymmetrical far-wing Doppler broadening of the Balmer lines from magnetron type discharges. Li-Ayers and Benesch [5] found that the magnitude of the far-wing profiles varied with cathode material as expected for reflection of the energetic particles responsible for excitation. May [6] used optogalvanic techniques to measure a Doppler broadened profile with a voltage dependent width for $H(n = 2)$ atoms in the cathode region of a Ne–$H_2$ glow discharge. These early observations illustrate the wide variety of laboratory experiments in which excess broadening is observed. More examples are cited in recent papers of this series [1–3]. The limited number of comparisons in this paper are chosen to illustrate various aspects of the model for pure $H_2$, i.e. a historically complete review is not attempted. This is an exploratory paper with a very much simplified discharge model that allows application to a wide range of experiments. The model will eventually need a better numerical treatment with more realistic geometries and using realistic differential collision cross-sections. Thus far, only results using very approximate differential cross-sections are available [7, 8].

The paper presents the simplest comparisons of calculations and experiment first, with the more approximate and less obvious comparisons later. Because of the complexity of the kinetics model, it is strongly recommended that readers first study the published model and experiments for uniform electric fields [1]. The paper begins with a discussion of representative electrode configurations and assumed electric-field distributions in section 2. The range of experimental parameters covered is then reviewed. The required modifications of the kinetics model of [1] are summarized in section 3. Calculated and measured spatial and spectral distributions of emission and ion-energy distributions are compared for planar cathodes in section 4 and for hollow or grid cathodes in section 5. Section 6 briefly discusses some related discharges that are not analysed. The appendices contain newly recommended cross-sections, a discussion of relevant space-charge effects and an improved empirical description of hydrogen atom backscattering from surfaces.

2. Discharge geometries and parameters

Because of the wide variety of electrode geometries considered, figure 1 shows a schematic of the adopted one-dimensional planar-electrode model superimposed on representations of actual electrodes. For the purposes of this paper the negative glow and the Faraday dark space are lumped together as a region of zero electric field [9]. This figure shows the approximate electrode configuration including a planar cathode and anode [10, 11], a planar cathode and a ring anode [10], a planar cathode and a hollow anode [8], a hollow cathode(s) and ring anode(s) [12, 13] or a cathode and anode constructed of wire grids [14]. The model places a planar anode at some representative position between the entrance to the hollow anode or the plane of the ring anode and the wall beyond these positions. In the hollow anode case [8], the emission data show considerable penetration of the discharge into the hollow anode. This also occurs for the wire electrodes [14]. Obviously, these geometrical approximations can influence the calculated emission, and eventually the correct geometry should be included in the models. Electron backscattering from the anode [15] is neglected.

Having related the planar electrodes of the model to the physical electrodes, the approximate electric fields used in the model are discussed. The model replaces the spatially varying electric field with a constant one-dimensional electric field in the cathode-fall region, and zero electric field in the negative glow and Faraday dark space [9]. The constant electric-field segments are estimates of the spatial average of the actual fields. Figure 2 shows examples of the measured [8, 10, 11] and assumed electric field $E$ to gas density $N$ ratios ($1 \text{Td} = 10^{-21} \text{V m}^2$). In cases where the field was not measured, e.g. [12, 13], the calculation uses the authors’ discharge voltage divided by a measured or scaled gas pressure times cathode-fall thickness [16].

A very wide range of discharge parameters has been [1–3] and will be covered. Figure 3 shows this range of conditions as a plot of average $E/N$ versus average discharge-current densities. The range of pressures and distances is relatively

\[ \frac{E}{N} \]

It is assumed that these authors show the spatial dependence of the fraction of $H(n = 3)$ atoms with an transverse energy greater than 1 Å (10.9 eV), not 10 Å as stated. The model of [1] shows that the heavy-particle fraction they derived earlier from this data gives a better measure of the emission caused by backscattered H atoms than their later approach. See Plain A, Barbeau C and Jolly J 1990 Ann. Phys. 15 Colloq. no. 3, 117. Their data have not been reanalyzed.
Figure 2. Measured (points) and approximate (lines) spatial distributions of electric field for Ganguly and Garscadden [11]—circles (blue), for Cvetanović et al [8]—squares (red), Barbeau and Jolly [10]—diamonds (green) and Dexter et al [45]. For the last three cases, the extent of the high-field region shown is equal to the stated cathode-fall thickness and the anode locations are well beyond the cathode fall.

Figure 3. Average $E/N$ in the cathode region versus discharge-current density for low-pressure hydrogen dc discharges considered in this review. The dashed line indicates the presence of significant (10%) space-charge distortion of the electric field, while the solid line shows the predicted transition to a fully developed cathode fall. These curves are for typical values of pressure times electrode spacing. The dotted lines indicate direct tests of the linear variation of the $H_\alpha$ excitation with discharge-current density.

These analyses neglect the build up of atomic hydrogen as the result of dissociation of $H_2$ by the discharge and the resultant increase in, for example, symmetric and asymmetric charge-transfer collisions of $H^+$ and $H^+_2$ with $H$ atoms. Measurements of fractional $H$ atom concentrations in rf discharges at input power levels comparable to those discussed in section 4 show hydrogen ground-state atom densities as high as several per cent [22]. These densities are dependent on highly variable surface recombination probabilities for $H$ atoms, especially for Cu [23]. It is estimated that $\geq 1\%$ of $H(1s)$ atoms are required for the symmetric charge-transfer collision of $H^+$ with $H(1s)$ to noticeably influence the present calculated results. Changes in the $H_2$ translational temperature caused by the discharge are neglected because of the high kinetic energies of the relevant collisions. The effects of increases in the $H_2$ vibrational temperature on electron attachment to $H_2$ are large [24] and, fortunately, can be neglected in this paper. These calculations adopt the custom of all the authors cited of neglecting possible changes in $H_2$ density resulting from temperature increases caused by the discharge.

3. Kinetics model

Most of the collision cross-sections, the transport and reaction equations and the numerical technique used in this present model are discussed in detail in [1]. Therefore, this section is concerned with kinetic processes that were not included in the earlier versions of the model [1–3]. Because the experiments

limited (0.2 $\leq pd < 3$ Torr cm) and a three- (or more) dimensional plot is not shown. The upward-pointing (blue) triangles represent the low-current, low-pressure experiments from which the spatial scans of $H_\alpha$ emission of [2] were selected and used primarily to test the reaction kinetics and absolute values predicted by the model. The group of downward-pointing (green) triangles represent the data sets from which the $H_\alpha$ Doppler profiles of [3] were selected and used to test the velocity distributions of the emitting species and the absolute intensity predictions of the model. These experiments were conducted at current densities of $< 10^{-2}$ A m$^{-2}$ for which the electric field is spatially uniform. For these conditions, the spectrally integrated magnitudes of the $H_\alpha$ signal were found experimentally to be a linear function of the discharge current for the parameters indicated by dotted lines [1, 17].

The dashed line of figure 3 shows the approximate upper limit to the $E/N$ for which space-charge effects can be neglected and the electric field is spatially uniform. See appendix B for the derivation of this condition. For sufficiently large electrode separations and experimental current densities, i.e. to the right of the solid line of figure 3, one expects a fully developed cathode fall [9]. This review includes the modeling of several such experiments [8, 10, 13, 18]. The available measured spatial dependences of the electric field [8, 11, 19] are shown in figure 2. For the hollow-cathode experiments [13, 18] there is considerable uncertainty in the estimates of the spatial distributions of both the electric field and the current. The averages of the $E/N$ between the cathode and anode for the experiments of Boris et al [14] and section 5.3 are too high to plot in figure 2. The range of current densities covered in direct tests of the linearity of $H_\alpha$ emission predicted by the model is extended as indicated by the dotted lines [20, 21].
be destroyed on collision with any surface. However, recent experiments with a graphite cathode [31] raise the possibility of a significant energy dependence of the H\(^-\) yield and of the role of adsorbed H\(_2\).

Next, the process of H(n = 3) production at surfaces is reconsidered. As shown in [1], this process is not expected to be observed at moderate H\(_2\) pressures. However, it will be found to be important at very low pressures and observations near a surface [32]. On the basis of experiments with hydrogen and deuterium ions for various surfaces [33, 34], the probability of H(n = 3) excitation per reflected H atom is assumed to be 0.1 at high energies, with the measured low-velocity cutoff [34].

A serious problem in the extension of the model of [1] to glow discharges is the treatment of radial losses, particularly in the negative-glow-Faraday dark space [9] in axially extended geometries. In these regions, fast H(n = 3) atoms are produced by fast H atoms previously reflected from the cathode, while slow H(n = 3) atoms are excited by electrons accelerated through the cathode fall. The problem of charged-particle loss from these regions has been treated recently by Donkó et al [35]. Based on the unpublished measurements of [25], the calculations of this review are made assuming that electrons are scattered through a large angle and are lost to the wall at a rate determined by the momentum transfer cross-section. The assumption of a concurrent loss of an ion resulting from the action of the ambipolar electric fields, created by the escaping electrons, on relatively low-energy ions has little effect on H(n = 3) excitation. An empirical alternative to loss by scattering is the loss of energy by the electrons, e.g. in section 4.3 a factor of 4 increase in the continuous energy-loss function of [36] would be required to fit the observed electron attenuation when large-angle scattering is neglected. Thus, it will be found that the apparent attenuation of the electron-excited portion (‘core’) of the H\(_a\) profile depends primarily on the electron loss. The attenuation of the wings depends on the initial diffuse emission of the reflected fast H atoms [1], on the subsequent radial scattering of the surviving fast H atom and on the collisional energy loss discussed in [1]. For a fixed pressure and discharge geometry, the relative magnitude of the cathode-leaving wing component of the H\(_a\) profile is varied by adjusting the fast atom reflection coefficient at the cathode. Because of the multi-step nature of the H(n = 3) excitation chain [1], the cathode-approaching wing of the H\(_a\) profile generated in the cathode fall increases rapidly relative to the core as the thickness of the cathode fall changes with discharge parameters.

The flux of positive ions, mostly H\(_2^+\), entering the cathode fall from the negative glow [9] is effectively limited by the radial flow to the wall of the electrons that produce the ions [25]. This H\(_2^+\) is partially converted to H\(_3^+\) and H\(^+\) by energetic collisions in the high electric field of the cathode fall.

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\(^{4}\) Experimental current growth measurements are used to determine effective ionization probabilities at very high E/N. Transient H\(_a\) emission data for conditions similar to those of [2, 3] agree with predictions based on the model of [1]. For example, the transient current and emission waveforms show the delays in emission expected for the multi-step kinetics model.

\(^{5}\) See files in the directories electronneutral and ionneutral at http://jila.colorado.edu/~avpcollision_data. The electron-neutral portion of the data is also part of the electron data compilation at http://www.lxcat.laplace.univ-tlse.fr/.
4. Experiments with planar cathodes

4.1. Experiments of Ganguly and Garscadden

Analysis of the experiments by Ganguly and Garscadden [11] considered in this section is the first step in testing the extension of the uniform electric-field model [1] to higher current densities and higher $E/N$. Their discharge current is 5 mA or 1 mA cm$^{-2}$ for an electrode separation of $d = 6.5$ mm and diameter of 25.4 mm at a pressure of $p = 0.3$ Torr and a discharge voltage of $V = 6.5$ kV. The discharge is an obstructed discharge [9] in which the measured electric field $E$, as shown in figure 2, varied only about 30% and the average $E/N$ is 55 kTd. Thus, the parameters for this experiment fall very close to the dashed curve of figure 3 marking the onset of space-charge effects. Figure 5(a) shows a comparison of calculated and measured spectral distributions of H$\alpha$ emission, while panel (b) shows comparisons of the spatial variations of the integrated components of H$\alpha$ emission versus distance from the cathode for a hydrogen discharge from Ganguly and Garscadden [11]. The present model assumes that the effects of electrons backscattered from the anode on the relative values of the H$\alpha$ emission are small [15].

Figure 5(a) compares the calculated H$\alpha$ profile (curve) and measured relative spectral distribution (points) for the H$\alpha$ line as observed perpendicular to the electric fields (transverse to the discharge axis). The points are adjusted in magnitude to roughly fit the calculations. The vertical dashed (red) lines show the authors’ choice of the dividing wavelength shift between large (wing) and small (core) Doppler shifts. The model profile is calculated assuming the earlier fit to the published fast heavy-particle reflection, the angular distribution parameter for reflected H atoms ($b = 0.6$) and the reaction probabilities of [1] with the addition of the non-equilibrium behavior of electrons discussed in section 3. Thus, the adjustable parameter in the comparison in figure 5(a) is the magnitude scale factor applied to the experimental data. The calculated shape of the wings of the profile is good, but their magnitude is too small relative to the core of the line. Also note that the experiment shows departures from cylindrical symmetry [11] that may account for the observed asymmetries in the profile.

The dashed–dotted (black) curve of figure 5(b) shows the calculated spatial distribution of the integral of the H$\alpha$ profile for $|\Delta \lambda| < 0.1$ nm, primarily caused by electron excitation. The dashed (red) curve shows the calculated sum of the contributions of fast excited H($n = 3$) atoms with $|\Delta \lambda| > 0.1$ nm, while the solid (blue) curve shows the total intensity. The relative intensity scale is adjusted by eye to fit the calculations. The large decrease with position in the calculated emission in the core of the H$\alpha$ line results from the radial loss of electrons as determined by the momentum-transfer cross-section for electrons discussed in section 3 and in [25]. As for experiments at low-current densities in [1], the present comparison with experiment assumes that the yield of reflected fast H atoms is that given by backscattering theory and experiment [1, 37, 38]. The agreement between the calculated and measured spatial intensity variations is moderately good, although there are systematic discrepancies that are not understood.

An interesting aspect of the obstructed discharge used by Ganguly and Garscadden [11] is the small number of collisions of ions, fast atoms and fast molecules with the background H$_2$ because of the relatively small $pd$, where $p$ is the pressure and $d$ is the electrode separation. Because of the multi-step kinetics leading to H$\alpha$ production, there is relatively little excitation by fast H atoms or H$_2$ molecules approaching the cathode, and the data provide an enhanced opportunity to study the behavior of H atoms backscattered from the cathode. Evidence for this behavior is that the predicted, but unmeasured, axial H$\alpha$ spectral profile is highly asymmetric for cathode surfaces with a high efficiency of fast atom reflection.
4.2. Experiments of Barbeau and Jolly

The extensive set of $H_2$ profiles transverse to the electric field from the experiments of Barbeau and Jolly [10] offers us an opportunity to (1) test the present model of the spatial and pressure dependence of the relative emission in the wings of the $H_2$ line, (2) possibly improve the model of the core of the $H_2$ profiles in the limits of excitation by H atoms and of excitation by electrons and (3) briefly review the evidence against a significant contribution to the $H_2$ and of excitation by electrons and (3) briefly review the evidence against a significant contribution to the $H_2$ and of excitation by electrons. Experiments of Barbeau and Jolly [10] at 1100 V and 0.27 Torr. Figure 6 shows the calculated fluxes of ions, atoms (long-dashed purple curve) is small and decays rapidly as that of the cathode fall. As shown in figure 2, Barbeau and Jolly [19] found that the electric field in the cathode fall at 0.6 Torr, 100 A m$^{-2}$, and 800 V decreases linearly with distance. Using their value for the product of pressure and the surprisingly large cathode-fall thickness [16] of $\approx 0.7$ Torr cm and neglecting variations with current density [16], the estimated average $E/N$ in the cathode fall varies from 2.1 to 4.6 kTd for pressures from 0.27 to 1 Torr. The use of a ring anode when making $H_2$ profile observations along the axis of the discharge make the effective cathode–anode distance and anode area indefinite. The model results are therefore normalized to charged-particle fluxes at the cathode.

The experiments of Barbeau and Jolly [10] are carried out at significantly larger pressures and distances than those of Ganguly and Garssadden [11]. This requires that the model deal with the contribution of the negative-glow region as well as that of the cathode fall. As an example of the predictions of the model, figure 6 shows the calculated fluxes of ions, atoms and fast molecules versus position for the lowest pressure experiment of Barbeau and Jolly [10], i.e. $p = 0.27$ Torr. The calculated fluxes are normalized to the electron flux at the cathode. In view of the relatively large radius of the discharge, it is assumed that all ions produced in the negative glow enter the cathode fall. Because of the low ion energies in the negative glow, the $H_2^+$ (dashed-orange curve) produced by electrons are rapidly converted to $H_2^+$ (dotted-green curve). When the $H_2^+$ enter the high electric field of the cathode fall, many are converted to $H_2^+$ and $H^+$ (dashed–dotted red curve). The $H^+$ flux produced at the cathode during the reflection of H atoms (long-dashed purple curve) is small and decays rapidly by collisional detachment. If one assumes that none of the ions produced between the ring anode and the cathode fall is injected into the cathode fall the ion and neutral species fluxes in the cathode-fall region are significantly smaller than with ion injection. An example of the case of no injection is the lower dotted (green) curve for $H_2^+$. Not surprisingly, the flux plots in the cathode-fall region for no ion injection are qualitatively similar to those calculated for the high $E/N$, uniform electric-field case in figure 7(a) of [1]. Near the cathode, where most of the $H_2$ is produced by the more energetic particles, the difference in fluxes for the two cases is only $\sim 10\%$ for $H_2^+$ and $\sim 40\%$ for fast $H_2$.

Figure 7(a) compares experimental and calculated examples of transverse profiles obtained by Barbeau and Jolly [10] at two positions along the axis of the discharge at a pressure of 1 Torr and a cathode–anode separation of 30 mm. These experimental profiles are normalized to the model, preserving the experimental relative magnitudes. Because the contribution of electrons is small at 1 mm from the cathode, the transverse profile shown by the upper curve of figure 7(a), is expected to be representative of emission by $H(n = 3)$ atoms produced by dissociative excitation [39] of $H_2$ by H atoms with energies in the 200 eV range. Empirically, the broad core for the $H_2$ line can be approximated by the following normalized dispersion formula:

$$I_0(\Delta \lambda) = (\pi w_d)^{-1}(1 + \Delta \lambda^2/w_0^2)^{-1},$$

where $w_d = 0.07$ nm is the half-width at half-maximum (HWHM) of this profile. When using this relation, it is necessary to increase the assumed fraction of H atom excitation leading to emission in the core of the line to about 50%, compared with the 10% previously assumed [1]. In the lower curve of figure 7(a) for data taken at 14 mm from the cathode, a better fit is obtained using a Gaussian function with a HWHM of 0.05 nm corresponding to about 3 eV atoms. This change in the core behavior correlates with the calculated increase in electron-induced dissociative excitation relative to excitation by fast H atoms at large distances from the cathode [8]. Obviously, further work is required to test these suggested fits.

In the calculation of the axial profiles in figure 7(b), it is assumed that the angular distribution parameter in equation (8) of [1] decreased with pressure from $b = 5$ for approaching $H(n = 3)$ atoms and $b = 1$ for leaving $H(n = 3)$ atoms at 0.27 Torr to $b = 0.2$ for all $H(n = 3)$ atoms at 1 Torr. Thus, good fits to experiment require one to assume that the angular distributions become significantly more isotropic as the pressure increases. The experimental axial profiles are independently normalized to the model. An unknown parameter of the model is the effective distance into the cathode fall. One logical choice would be a distance determined by $\Delta \lambda = 0.6$ nm that are just below the noise level of the available data.

\[6\] The dispersion width of $w_d = 0.07$ nm (HWHM) corresponds to an exponential decay of an excited state with a lifetime of $\sim 1.6 \times 10^{-12}$ s. This time is much longer than the duration of a typical H + $H_2$ collision or of the resultant $H_2$ dissociation and much shorter than a typical radiative lifetime. Therefore, no particular significance is given to the empirical dispersion profile. The calculated solid curve for $\gamma = 1$ mm shows wings of the dispersion profile at $|\Delta \lambda| > 0.6$ nm that are just below the noise level of the available data.
the balance between diffusion to the cathode-fall boundary and loss by radial diffusion by electron–ion recombination [9, 35]. Empirically, the calculations assume negligible ion flux entering the cathode fall. This assumption improves the agreement with the shape of the profiles that are emitted with wavelength shift greater than 0.1 nm.

The effects of heavy-particle-induced ionization and ion-pair formation in collisions of the fast atoms, ions and molecules with H2 are modeled using the cross-sections summarized in appendix A. The addition of these processes increases the spectral intensities shown in figure 7(b) at $\Delta \lambda < -0.2$ nm by $\sim 10\%$ at both 0.27 and 1 Torr. For $\Delta \lambda > +0.2$ nm, the addition of these processes increases the calculated intensities by $\sim 10\%$ at 0.27 Torr and $\sim 30\%$ at 1 Torr.

The measurements of the relative intensities of the core and wing components of the transverse Hα profiles by Barbeau and Jolly [10] shown in figure 8 provide a further test of the ability of the model to predict the apparent attenuation of the $H(n = 3)$ atoms as one moves away from the cathode. This figure shows the measured and calculated fractions of the profiles that are emitted with wavelength shift greater than 0.1 nm, i.e. the fraction of the profile emitted by $H(n = 3)$ atoms with greater than 10.9 eV energy along the line of sight. This fraction is a measure of the relative importance of $H_\alpha$ excitation in the wings resulting from heavy-particle collisions with $H_2$ versus $H_\alpha$ excitation in the core by electrons and heavy particles. The comparisons of calculations and experiment in figure 8 show that the model correctly predicts the change in the ratio of the core and wing components of the Doppler profiles with pressure.

In summary, the observations of Barbeau and Jolly [10] are quantitatively explained in terms of excitation of the wings of their $H_\alpha$ profiles by fast H atoms and $H_2$ molecules produced by ions approaching the cathode, plus excitation by fast H atoms produced on reflection at the cathode of ions, atoms and molecules.

4.3. Experiments of Cvetanović et al

This section compares the predictions of the extended model with some of the many measurements of $H_\alpha$ emission from $H_2$ glow discharges by Konjević and coworkers [8, 21, 40–43]. Using high-resolution measurements of the Balmer series profiles, Cvetanović et al [8] determined the electric field in the cathode region as shown in figure 2 for their 0.29 Torr, 900 V discharge. The simplified model of this paper utilizes the average field. The approximation made in section 2 in which the hollow cylinder anode is replaced by a planar anode seems reasonable in view of the small thickness of the cathode fall (1.6 mm) compared with the internal diameters of the anode (5 or 8 mm) and the very small electric field expected in the negative glow [9]. The effective anode is placed at the maximum distance from the cathode for which data are shown. The distortion of the electric field in the portion of the negative glow located inside the hollow anode is neglected. All the model results of this section are normalized to unit total charged-particle flux at the cathode. Because of the reported severe damage of the cathode by particle bombardment [44], model calculations multiply the reflected H atom flux from
Figure 9(a) shows a comparison of calculated and measured Doppler profiles observed transverse to the discharge axis in the negative-glow region at the positions indicated in figure 10. The points show the experimental data of Cvetanović et al [8] plotted with the same scale factor for the two profiles. The principle contributions to the calculated emission by $H(n = 3)$ atoms are from excitation by fast $H$ and by fast $H_2$. The contributions of $H_\alpha$ excitation caused by $H^+$, $H^+_2$ and $H^+_3$ approaching the cathode are small. The ‘core’ component is mostly from excitation by electrons, plus some dissociative excitation by fast $H$ and $H_2$. As in [1], the electron excitation portion is assumed to be 50% dissociative excitation with an effective HWHM of 0.05 nm (3.5 eV) chosen to fit these experiments. The remaining dissociative electron excitation is assigned an effective full-width-at-half-maximum (FWHM) of 0.01 nm to simulate the fine structure splitting and Stark broadening [41]. As the point of observation is moved away from the cathode, there is a relative decrease in the excitation in the wings resulting from the loss of diffusely backscattered fast $H$ atoms. Here it is assumed that the effective reflection coefficients for the highly sputtered Cu cathode are 30% of predicted values [37]. As in the case of the upper transverse profile of figure 7(a), the assumption of Gaussian profiles for the broadening of the core does not yield good fits to the experimental profiles near $\Delta \lambda = \pm 0.2$ nm. The empirical fits of modified dispersion profiles discussed in section 4.2 have not been tested against the present experiments.

Figure 10 shows a comparison of calculated and measured spatial distributions of the components of $H_\alpha$ emission obtained by fitting three Gaussians to the profiles measured transverse to the discharge axis at various points along the discharge. The area under the widest Gaussian, called $G_3$ by these authors [8], comes much closer to representing the contributions to the $H_\alpha$ profile resulting from fast $H(n = 3)$ atoms, some of which move along the discharge axis and have low transverse velocities, than does selection of high radial energy $H(n = 3)$ atoms used by other authors [10, 11]. The sum of the areas under the two narrower Gaussians ($G_1 + G_2$)
then represent the \( H_2 \) excitation resulting from dissociative excitation of the target \( H_2 \) by electrons and by incident fast heavy particles. This sum is the core of the line in this paper. In the model it is assumed that the reflection as \( H \) atoms is 70% of the predicted values for Cu [37], probably corresponding to a relatively undamaged cathode. This reflection parameter primarily determines the relative magnitude of the reflected- or leaving-atom component responsible for the wings of the profile in the negative glow, i.e. the (red) curve of figure 10. As pointed out by the model of Cvetanović et al [8, 43], these data show that the diffusely reflected fast \( H \) atoms from the cathode are lost much more rapidly than the beam-like electrons injected into the negative glow from the cathode fall.

The reasons for the discrepancy between the model and experiment for the spatial dependence of emission within 1 mm of the 6 mm diameter Cu cathode are unknown. Similarly, the differences among the data for the various lines of the Balmer series in this region are unexplained. A structure in the total emission similar to that observed near the cathode can be obtained by subtracting the \( H_n \) emission attributed by the model to excitation by approaching heavy species, i.e. excitation by fast \( H \) and \( H_2 \), and shown by the dashed-dotted (green) curve in figure 11. However, the analysis of section 5.1 presents reasonably direct evidence of a significant contribution by both fast \( H \) and fast \( H_2 \) to excitation of \( H(n = 3) \) atoms approaching the cathode.

The comparison of the predictions of the present model with the Doppler profiles shown in figure 2 of Gemišić Adamov et al [21] for various cathode materials is satisfactory for the Au cathode. However, the predicted wings of the \( H_2 \) lines are much larger than observed for their graphite cathode (not shown here). This reference provides another important test of the present model, i.e. the predicted linear dependence of the various components of the Doppler profile on the discharge current is verified by the data of their figure 6. The associated \( E/N \) and \( J \) range is shown in the present figure 3. The papers by this group have argued for the importance of \( H_2^* \) ions formed from collisions of \( H_2^* \) with \( H_2 \) in the reaction sequence resulting in \( H_2 \) excitation. The model predicts a relatively small fraction of the excitation is by \( H_2^* \) collisions with \( H_2 \), but figure 4 and figure 1 of [1] show that \( H_2^* \) formation and destruction play an important role in the ion, atom and molecule reaction sequence that leads to \( H(n = 3) \). In summary, the model of this work provides quantitative fits to many, but not all, aspects of the \( H_n \) emission profiles and spatial distributions measured by Konjević and coworkers.

4.4. Experiments of Dexter et al

The experiments of Dexter et al [45]\(^7\) test the ability of the model to predict the relative ion fluxes and ion-energy distributions for \( H^+ \), \( H_2^+ \) and \( H_3^+ \) reaching the cathode of a low-pressure discharge in \( H_2 \). These authors used a mass spectrometer to measure relative ion currents for a glow discharge operating at 2 Torr, 530 V and a current density of 2.5 A cm\(^{-2} \). The length of the cathode fall determined from

\( n = 3 \). In summary, the model of this work provides quantitative fits to many, but not all, aspects of the \( H_n \) emission profiles and spatial distributions measured by Konjević and coworkers.

\(^7\) Based on their figure 15, we have assumed that their stated dimensions of the alumina separator are interchanged.

![Figure 11. Measured and calculated ion-energy distributions at the cathode for \( p = 2 \) Torr and \( V = 530 \) V from the experiments of Dexter et al [45]. The points are from their experiment and the dotted curves are smoothed fits to the Monte Carlo results of Dexter et al. The smooth curves are predictions of the present model.](image-url)
5. High-voltage, hollow-cathode discharges

The discharges of interest in this section are perhaps better characterized as ‘transparent-cathode’ discharges than hollow-cathode discharges in the textbook sense of electrons oscillating radially in the space-charge potential well inside the cathode [9, 49]. The transition from the conventional hollow-cathode mode to the high-voltage, low-pressure mode for H2 discharges is discussed by Lavrov and Mel’nikov [12, 18]. According to their qualitative observations, as the pressure is reduced the region of highly visible emission moves from the interior of the hollow cathode to the space between the end of the cathode and the anode. Although the discharge tube is constructed with a ring anode aligned with each end of the hollow cathode, only one anode is electrically connected. The model of this experiment is simplified by making the assumption that at the pressures of interest the tubular cathode can be replaced by a highly transparent planar cathode. This simplification is illustrated in figure 1. The Heα radiation produced inside the hollow cathode is neglected. The Heα profiles of figures 2 and 3 of Lavrov and Mel’nikov [12] and figure 9 of Šišović et al [42] for low-pressure, hollow cathodes clearly show the high asymmetry resulting from the reduced backscattering expected for a relatively transparent cathode. These comparisons are followed by discussions of somewhat similar discharges in electrostatic-confinement devices [13, 14, 32].

5.1. Experiments of Lavrov and Mel’nikov

The data of Lavrov and Mel’nikov [12, 18] are of interest because of the voltage and pressure dependence of their results, their evidence for excitation by at least two species, and the authors’ proposal that their results show the importance of negative ions. These authors noted that their Doppler profiles have a relatively weak Heα wing extending to positive wavelength shifts well beyond values expected for H atoms backscattered from H2 molecules. They attribute this observation to excitation of Heα by H− ions. Consequently, the present model has been extended to include H− production and loss as described in section 3 and appendix A. Šišović et al [42] have also observed similarly highly asymmetric Heα profiles and, in addition, have shown the reversal of the asymmetry with the direction of the applied voltage expected for an electric-field-dependent excitation and discharge model, such as that of this paper.

Figure 12 shows examples of the Heα profiles observed by Lavrov and Mel’nikov [12] observed along the axis of symmetry of their discharge, i.e. along the electric-field lines of the simplified model. The relative magnitudes of the experimental profiles for 0.09 and 0.58 Torr are normalized to current and pressure and then plotted with the same scale factor. The corresponding estimated cathode-fall lengths vary from 25 to 4 mm and the cathode to anode separation is taken to be 50 mm. The calculated curves show good agreement with the experiments covering factors of 3.5 in voltage and 6 in pressure. As in previous sections, the intensity at negative ∆λ is attributed to excited H(n = 3) atoms excited primarily by fast H atoms and fast H2 molecules moving toward the cathode, while the intensities at positive ∆λ are attributed to fast H(n = 3) atoms excited by fast H atoms reflected from the cathode. The relatively small flux of H atoms reflected by the edge of the cathode is treated as a semitransparent cathode effect, i.e. the model assumes that the infinite diameter cathode has a reflected H atom yield of ≈50% of that expected for a planar Fe cathode as given in appendix C. The fits of the model to experiment in figure 12 show the expected need to assume a more diffuse angular distribution as the pressure is increased, i.e. the assumed angular distribution parameter b for approaching fast H atoms is reduced from 10 for 0.09 Torr to 1 for 0.58 Torr. At the highest pressure of 0.58 Torr the wings of the measured profile in figure 12(c) seem to extrapolate smoothly from positive to negative wavelength shifts. This observation suggests the possibility that multiple scattering and/or large-angle scattering events in the excitation chain can cause ions that are initially moving toward the cathode to produce...
excitation of $H(n=3)$ atoms moving away from the cathode. Similarly, fast atoms reflected from the cathode may result in $H(n=3)$ atoms moving toward the cathode. Such events are not included in the present model.

The broken curves of figure 12(a) through (c) show that calculated $H_2$ excitation is principally by fast $H$ (solid blue curves) and by fast $H_2$ (dashed–dotted green curves). The excitation by all ions (dashed purple curves) is significantly smaller. In figure 12(b), the peak in the dashed–dotted (purple) curves near $\Delta \lambda = -0.5$ nm is caused by $H_2^+$ and $H_2^+$ ions, while the shelf near $-0.7$ nm is caused by $H^+$ ions. Thus, the presence of two peaks in the total emission in panel (b) near $\Delta \lambda = -0.6$ nm for 0.19 Torr results from the shifting relative importance of excitation by fast $H$ atoms and by fast $H_2$ molecules with pressure. The peak from excitation by ions, especially $H_2^+$ ions, tends to hide the minimum. Note that because of the large symmetric charge-transfer collision cross-section, the $H_2^+$ peak occurs at roughly the same $\Delta \lambda$ as the peak resulting from excitation by $H_2^+$. As suggested by the calculations of figure 6 and the discussion by Dexter et al [45], the model shows that most of the $H_2^+$ produced in the low electric-field (negative-glow) region by electron collisions with $H_2$ are converted to $H_2^+$ and that much of this $H_2^+$ is converted back to $H_2$ when the ions reach the high-field region.

The proposal by Lavrov and Mel’nikov [12] that production of $H_2$ excitation by $H^-$ ions is significant at positive $\Delta \lambda$ is investigated. See appendix A for a summary of relevant cross-sections. Using a representative surface yield of 0.04 $H^-$ ions per backscattered $H^+$ atom one obtains the $H_2^+$ profile at positive $\Delta \lambda$ shown by the dashed–double dotted (dark red) curves in figure 12. Because of the very large loss of $H^-$ by collisional detachment at the relatively high pressures of these experiments, this emission is small and is shown after multiplication by a factor of 100 [50]. At 0.19 Torr, the contribution to the $H_2^+$ excitation by $H^-$ produced at the cathode surface is $\sim 70\%$ of the total. The contribution by $H^-$ produced by ion-pair formation in the high-field region is $\sim 25\%$ and that by dissociative attachment by electrons primarily in the low-field, negative-glow region is $\sim 5\%$. While $H^-$ production by electron capture by reflected fast $H$ atoms leaving the cathode surface can result in $H^-$ with energies up to twice the applied voltage, the model shows little contribution to the $H_2^+$ profile for energies above that corresponding to the applied voltage. These calculations neglect the potentially important, but unknown, flux of $H^-$ ions emitted by the hollow cathode that would appear with a maximum energy determined by the applied voltage. Thus, the model suggests that $H^-$ induced excitation of $H_2$ has not been observed in these experiments.

5.2. Experiments of Kipritidis et al

In this section the kinetics model is applied to the Doppler profiles obtained from the low-pressure, hollow-cathode experiments as described by Kipritidis et al [13, 32]. These ‘inertial electrostatic-confinement’ discharges are designed to build up high densities of fast hydrogen (deuterium) ions and neutral species by trapping the positive ions in a potential minimum created by the hollow cathode. These discharges are assumed to be symmetrical about the center of the hollow cathode, although they sometimes are not. The hollow cathode is replaced with partially transparent planar cathodes at each end of the actual cathode. The ring or mesh anodes are replaced with partially transparent planar anodes. The model does not solve for the discharge behavior inside the cathode, but instead assumes that the ions that strike the surface of the cathode give rise to an electron current that is effectively emitted at the ends of the cathode [51]. In a simplification suggested by previous studies of these discharges [13, 32], it is assumed that the unknown potential inside the cathode is spatially uniform and at some adjustable fraction of the applied potential [52]. Child’s law formulae from appendix B are used to estimate the thickness of the axial cathode sheath adjacent to the ends of the hollow cathode, as illustrated for more conventional discharges in figure 2. The discharge conditions are similar to those of section 5.1, except that the hydrogen pressures are significantly lower and surface effects can become dominant.

The actual calculations assume that the discharge occurs only on the right-hand side of the symmetrical electrodes, where the directions are appropriate for figure 1. The asymmetric results are then reflected about the center. In this asymmetric model, the positive ion flux moving leftward toward the cathode builds up from zero at the wall as the result of a nearly uniform electron flux moving to the right toward the anode as expected for a low–pressure version of figure 6. The original ions are mostly $H_2^+$ near thermal energies and are partially converted to $H_2^+$ ions. Once these ions drift to the high-field region of the cathode fall, many of the $H_2^+$ ions are converted to $H_2^+$ and $H^+$, which then produce fast $H_2$ and $H$. Once past the cathode, the leftward moving ions, but not the fast atoms, turn around in the decelerating electric fields. The assumed (but not verified) significant loss of positive ions to the inside wall of the cathode reduces the effects of positive-ion trapping. Fast $H$ is produced by particle reflection at the semitransparent cathodes located at the cathode edges and, especially, at the vacuum-chamber wall.

Figure 13 shows a comparison of calculated and measured Doppler profiles from Kipritidis et al. The experimental data points in panels (a) and (b) from [13] are for pressures of 23 and 35 mTorr, while the experimental profile in panel (c) is from [32] for 5 mTorr. For the first two pressures, the assumed symmetry of the model is a considerable simplification of the rather asymmetrical anode configuration employed [13]. The model potential changes from a constant value inside the cathode to a high constant field in the cathode-fall sheath and to a constant value outside the sheath. From appendix B, the sheath thicknesses are assumed to be 10, 15 and 40 mm for pressures of 35, 23 and 5 mTorr. The cathode to anode distance and the vacuum-chamber radius are assumed to be 100 and 240 mm.

The experimental observations in panels (a) and (b) of figure 13 were made looking through the ring anode at an angle of $25^\circ$ with the discharge axis, such that one does not observe radiation from the point of intersection of the
Figure 13. Comparison of calculated and measured axial Doppler profiles from Kipritidis et al. The experimental points of panels (a) and (b) are for the geometry of figure 3 of [13] and those of panel (c) are from figure 6 of [32] for the geometry of the associated figure 3. The smooth curves show calculations discussed in the text.

electron and particle beams with the wall. The calculated H₂ profiles are shown by the solid (red) curves, while the broken curves show various contributions to the total. The points are sampled from the experimental data. The agreement between the shapes of the solid curves and experiment is good except for the magnitude of the narrow core, where electron impact excitation dominates. The source of the discrepancies in relative magnitudes of the cores and the wings for these profiles is unknown, but not surprising in view of the use of one-dimensional geometry, etc. In these calculations, the off-axis observations are approximated by adding the axial and transverse contributions calculated using the procedures described in section VA of [1] and applied separately in previous sections of this paper. The calculated axial, transverse and core contributions are shown by the broken curves of panel (a). The intensity at Δλ > 0.2 nm is primarily from fast H(ν = 3) atoms seen by the observer as moving away from the cathode along the discharge axis. The dashed curves of panels (b) and (c) show that the contributions of excitation by fast H atoms and by fast H₂ molecules are comparable. The large contribution shown by the dashed–double-dotted (purple) curve in panel (c) is discussed below. Further tests show that the faster excited H atoms are the result of electron collisional ionization between the cathode and the mesh, while nearer the line center the excited atoms are the result of electron induced ionization between the cathode and the ring anode. Note that because the fast H⁺, H₂⁺ and H₃⁺ ions are created in the potential well near the cathode, they cannot reach the observation region and cause excitation directly. In the present model of these experiments, the excited atoms decay by emission much too rapidly to move from the high-field region or the wall to the observation point. See appendix B of [1] and [2].

The dashed (green) curve of panel (a) of figure 13 shows that the observed Hₑ for negative wavelength shifts is the result of motion of the H(ν = 3) atoms perpendicular to the axis of the discharge. As in the previous models [1, 3], this traverse motion is attributed principally to the diffuse angular distribution of H atoms leaving surfaces as the result of bombardment by, in the present case, fast H atoms and H₂ molecules. The model does not calculate the diffuse angular distributions, but uses the adjustable parameter b determining the angular distribution adjusted to best fit experiment [1], i.e. b = 0.6 for H(ν = 3) leaving the cathode and b = 10 for beamlike H(ν = 3) approaching the cathode. The magnitudes of the experimental data in figures 13(a) and (b) are shown with the same scale factor, i.e. they have not been normalized to take into account the expected scaling of roughly a factor of four from their products of current times pressure. Thus, the apparent agreement in the relative magnitudes of the wings of these profiles with the model is not understood.

The experimental Hₑ profile shown by the points in panel (c) of figure 13 is for the very low pressure of 5 mTorr and for a very high applied voltage of 30 kV. It shows observations made near the vacuum wall, looking toward the wall and at an angle of 30° with the discharge axis. An assumed cathode-fall voltage of 12 kV gives the best fit of the model to the experimental profile. The calculated emission observed at positive values of Δλ is the result of the excitation of H(ν = 3) atoms by fast H atoms and H₂ molecules approaching the wall, as shown by the dashed (green) and dashed–dotted (blue) curves, respectively. Most of these fast neutrals were produced by charge transfer from their analogue positive ions in the region of the potential well. Again, fast positive ions cannot reach the point of observation. Of particular importance for this experiment is the conclusion that the calculated emission at negative Δλ is primarily the result of H(ν = 3) atom formation as the backscattered fast H atoms leave the surface of vacuum-chamber wall. The process is discussed in section 3. Because the model shows that the excited atoms do not move significantly before radiating, this wall excitation process is generally not observed. The contributions of the axial and transverse components (not shown) are comparable, with the axial component more important at the larger positive frequency shifts and the transverse component at the larger negative shifts. Increasing the cathode-fall voltage to 27 kV in the model gives roughly the observed profile width in the far wings, but yields much too flat a profile nearer the line center.

The model is also used to examine the possibility of explaining the far-wing ‘shelves’ at positive and negative Δλ beyond 2.2 nm as the result of excitation of H(ν = 3) by fast H⁻ ions. The H⁻ ions are formed when fast atoms are

![Graphical representation of figure 13](image-url)
reflected from the wall, by dissociative attachment, and by ion-pair formation. Using estimated cross-sections, etc. discussed in appendix A, the calculated emission is much too small. Negative ion production inside the hollow cathode is also a possibility. However, only H− produced as fast H atoms leave the cathode surface can excite H(n = 3) atoms with energies higher than the that corresponding to the applied voltage.

5.3. Experiments of Boris et al

In this section the predictions of the kinetics model are compared with the measured energy distributions for D− ions and with estimated ratios of negative ion and electron fluxes from an electrostatic-confinement device described by Boris et al [14]. The reader is referred to the very extensive published discussions, e.g., the recent results in [14, 53]. Positive ions are injected at the anode and move through a potential with a central minimum, such as shown schematically in figure 14(a). This potential, to be used in the model below, does not include details such as the potential wells surrounding the individual grid wires. If the injected ions lose small amounts of energy they are trapped in the potential well at relatively high kinetic energies. These trapped positive ions oscillate in the potential well, occasionally producing fast atoms, molecules or nuclear reactions. Eventually the fast ions collide with the grid wires or undergo charge exchange collisions and drop to low kinetic energies. The low-energy ions are collected by the cathode grid wires. The roughly uniform potential distribution inside the cathode grid resulting from ion space charge, is sometimes referred to as a ‘virtual anode’ [53], because it is positive relative to the grid wires. In the present approximation, the equipotential region serves as a ‘virtual cathode’ relative to the anode grid.

In the spherically symmetric device being modeled, the central cathode consists of a highly transparent grid of 10 cm diameter. The anode is a concentric grid of 45 cm diameter, centered in a cylindrical Al vacuum chamber of 91 cm diameter. The geometrical transparency of each grid is assumed to be 0.95. In order to simplify the application of the present kinetics model, the spherically symmetric discharge grids are replaced by partially transparent planar electrodes in the one-dimensional geometry of section 2 and figure 1. As shown in figure 14(a), the model assumes a spatially uniform electric potential inside the grid. This potential plateau is chosen to give the best fit to experiment and will turn out to be significantly smaller than the applied potential, as is often postulated for such devices [53]. The electric field immediately outside the cathode grid is shown in figure 14 to be a region of constant electric-field strength beginning at the grid for a distance of 6 cm. It is only a rough approximation to the space-charge-free potential expected from the considerations of appendix B and figure 3 [53]. At larger distances, the electric field is assumed to be zero on the scale of the energy grid of the calculation. The presumed electric-field variations outside the anode grid resulting from biasing the filament and the vacuum wall so as to inject ions into the cathode region are accounted for by assuming that the injected ions drift inward toward the anode grid and that outward moving positive ions are reflected back through the anode and cathode grids. In order to obtain a stable numerical solution to the particle flux equations for the assumed geometry, the assumed transmission of the cathode grid for the lowest energy trapped ions is kept below 0.4311. The cathode and anode grid transmissions for higher energy ions are assumed equal to their geometrical value of 0.95. In spite of these rather drastic simplifications, the model serves to illustrate the dominant collision and transport processes leading to H− production under these extreme conditions. The cross-sections and product energy distributions for the H− formation process are discussed in appendix A.

In the following comparison of model results with experiment it is assumed that all aspects of the model developed for hydrogen apply directly to deuterium. Although this assumption is certain to lead to quantitative errors, there are not expected to be qualitative differences. Figure 14(b) shows calculated spatial distributions of the sum of the magnitudes of the left- and right-directed particle fluxes for the case of 2 mTorr pressure and 70 kV applied voltage presented in figure 4 of [14]. These calculated fluxes are normalized to unit positive-ion flux entering at low energies at the anode grids. The large normalized fluxes calculated for H2+ and H+ are misleading because more than 90% of these ion fluxes are in the lowest energy bin of the model and do not have sufficient energy to form H−, etc. A better measure of the effectiveness of the ion trapping is to note that the calculated H2+ and H+ fluxes inside the cathode and having energies above the lowest energy bin (1500 eV in our numerical scheme) are each about equal (±20%) to the total ion flux injected at the anode.

The results plotted in figure 14(b) show that the dominant ion is H2+ and the dominant fast neutral is the H2 molecule. The calculated results are insensitive to the proximity of the assumed value of the grid transmission for low-energy ions to the value causing numerical instability. The electron flux is calculated from the ion fluxes striking the cathode grid [54] using the assumed grid transparency and the electron yield per H+ ion for Mo [55], which is chemically similar to the W (but not Re) used experimentally. This figure also shows that the calculated ratio of the H− flux to the electron flux is ~0.3% compared with the experimentally estimated value of ~3% [14]. This result is very insensitive to the assumed grid transmission. For the present parameters, the discharge is sustained by the external ion source. Heavy-particle ionization makes an important contribution to the ion production, but is not sufficient to balance losses as assumed by Emmett et al [53].

The principal observable in this experiment is the energy distribution of H− ions as measured by an energy analyzer at the vacuum-chamber wall. The points of figure 14(c) show the measured energy distribution for H− ions for an applied voltage

10 Some of the cross-sections utilized by these authors for deuterium are rather different that those used in this paper for hydrogen.

11 Efforts to influence the transparency for the lowest energy ions at which the instability occurs have failed, e.g., changes in the assumed charge-transfer cross-sections for H2+ and H+ have no effect. On the other hand, one expects a higher efficiency of positive-ion collection by the grid wires for low-energy ions. The energy bin width for these numerical calculations is typically 1500 eV.

12 Contrary to these authors, the production of ions by electrons is found to be negligible for the conditions considered in this paper.
of 70 kV at a pressure of 2 mTorr. Boris et al [14] attribute the peaks in their measured energy distribution near 40 keV and 50 keV to H⁻ formed in collisions of H⁺ and H⁺ with H₂, respectively. The calculated energy distribution gives a series of very sharp peaks superimposed on a background. For purposes of comparison with experiment, the calculated curves have been folded into a Gaussian, such as might arise from local spatial variations in the electric potential. The energy analyzer is assumed to effectively sample the H⁻ flux reaching the anode grid. The model makes no allowance for possible spatial or energy variations in the H⁻ detection efficiency in the experiment. The dashed (red) curve of figure 14(b) shows that most of the H⁻ is formed in collisions of fast H atoms with H₂. The dotted (brown) curve shows that there is a significant contribution to the ≈40 keV peak from particle reflection at the surfaces of cathode grid wires. The dashed–dotted (olive) curve shows that H⁻ production in H⁺ + H₂ collisions makes a significant contribution to the peak near 59 keV. Production of H⁻ in fast H₂ and H⁺ collisions with H₂ are smaller and production by H⁺ is too small to plot.

The energy scale of the calculated peaks in figure 14(c) is set by assuming the effective plasma potential plateau inside the cathode grid to be ≈40 kV negative relative to the anode grid wires and vacuum wall. The fit is much worse if the potential plateau is assumed to be below the anode potential by the applied 70 kV. The decrease in H⁻ flux at energies above the high-energy peak at ≈58 keV is in qualitative agreement with experiment. Calculations show that the ≈58 keV peak increases in magnitude relative to the ≈40 keV peak as the applied voltage increases, as is observed in the experiments [14]. The model also shows a decrease in relative magnitude of this higher energy peak with increasing pressure as shown in figure 7 of [14]. However, the model fails to predict the observed ratio of peak heights for the ≈40 and ≈58 keV peaks.

Prominent features of the calculated H⁻ energy distributions are the low-energy peaks, e.g., those near 15 keV in figure 14(c). If the energy analyzer is assumed to effectively sample the H⁻ beam at the outer edge of the high-field region rather than at the anode as assumed in figure 14(c), the H⁻ flux at energies below ≈40 keV is reduced by more than an order of magnitude. This change occurs because the low-energy peaks are the result of H⁻ formation principally by fast H atoms in the space between the high-field region and the vacuum wall. Note that this region is calculated to be free of energetic positive ions. The model does not reproduce the very small relative values of H⁻ flux found at the lowest energies reported experimentally [14], i.e., just below the ≈40 keV peak.

A much more thorough analysis of the model and experiments is necessary to ensure the applicability of the model. For example, the calculated energies and relative magnitudes of the peaks in the H⁻ energy distribution are systematically shifted relative to experiments. No attempt has been made to estimate the role of nonlinear processes, such as charged-particle recombination or nuclear reactions involving collisions between energetic particles [53]. Spatial and spectral scans of the Hα emission should help define some of the geometrical and electrical parameters, as shown by the analyses in sections 4.2, 4.3 and 5.2. As shown throughout this paper, the wings of the Hα profiles are good diagnostics for high-energy hydrogen particles.

6. Other experiments

Babkina et al [56] determined the energy spectrum and enhanced far-wing of Hα emission of fast H atoms produced by various hydrogen ions when backscattered from a stainless steel surface biased negatively with respect to a microwave plasma source. Their Hα profiles also provided evidence of H⁻ formation from energetic hydrogen reflected from their negative electrode. The present model does not apply to their experiment because it does not have a sufficiently developed database for collisions in H₂–Ar gas mixtures.
The shape of the $H_n$ profile seen with an optical probe at large distances from the cathode by Bharathi et al. [57] is similar to the axial profiles of Barbeau and Jolly [10] at about the same pressure and discharge voltage (see section 4.2). Bharathi et al. discuss the various reactions and excitation processes, but do not calculate $H_n$ profiles. Because of expected strong departures of their discharge from one-dimensional geometry when the optical probe is moved to their ‘near cathode’ position, no attempt has been made to model their $H_n$ profiles.

Another type of dc glow discharge in hydrogen is the ‘hollow cathode’ with an internal anode examined by the mass spectrometer studies of Méndez et al. [47]. These authors analyze their results in terms of ion–molecule reactions that take place at energies determined by the wall temperature. They argue that one can neglect reactions of energetic hydrogen species in the cathode sheath or in the effusive gas flow region. No attempt has been made to adapt the present model to these experiments.

Next, consider pure hydrogen discharges in which ions are drawn from a plasma, accelerated, strike a planar cathode and may be sampled by a mass spectrometer. Some examples are Heim and Stori [58], Halliwell et al. [59], Gans et al. [60], Babkina et al. [56] and Schiesko et al. [31]. In general, one expects the average energies of the ions in the discharge source to be a few eV as determined by the ambipolar field generated by the electrons. These discharges produce $H_2^+$ by electron impact and, except at very low pressures, the low-energy $H_2^+$ are rapidly converted to $H_3^+$. The kinetics model of this paper is particularly appropriate for predicting the further reactions that occur in the space-charge sheath, but no comparisons have been attempted.

The few dc experiments of Mills et al. [61] and Phillips et al. [62] for pure $H_2$ are not useful for quantitative testing of models of the source of fast $H(n = 3)$ atoms emitting far-wing $H_n$ radiation. For example, the $H_n$ profile of figure 14 of [63]13 was obtained at an unknown pressure and unknown position relative to the beginning of the negative glow. The best one can say is that this profile is qualitatively similar to the transverse profiles of figure 7(a) and figure 9(b). This author does not know of any discrepancies between the predictions of the present model and their qualitative experimental results for dc discharges in hydrogen. It is expected that an extension of an electric-field-based model will explain well-characterized measurements of $H_n$ profiles in their rf discharge geometries, e.g., figure 9 of [64]14.

Other hydrogen plasmas to which the present kinetics model is expected to be applicable are the aurora observed in the hydrogen-rich outer planets [65] and controlled fusion plasmas, especially as one approaches the walls [66]. However, no examples have been analyzed that illustrate this applicability because of the difficulty in constructing simple models of the very complex geometries, the spatial and temporal fluctuations of the electric and magnetic fields and the variations in gas composition and densities.

7. Discussion

The comparisons of model predictions with experiment in this paper have demonstrated the usefulness of a simplified model of the kinetics of energetic hydrogen ions, atoms and molecules for quantitatively explaining observations of $H_n$ emission from low-pressure $H_2$ discharges ranging from short-gap, parallel-plane discharges; through glow discharges of various geometrical complexities; to beam-like, electrostatic-confinement discharges. The comparisons have emphasized the shapes of $H_n$ Doppler-broadened profiles, relative spatial distributions of spectrally integrated emission and the energy distributions of mass-identified ion fluxes at the cathode. Similarly successful comparisons of predicted and measured absolute emission at low-current densities have been made earlier [1–3].

The comparisons of calculated and observed $H_n$ profiles and spatial distributions show the importance of $H(n = 3)$ excitation in collisions of fast $H$ and fast $H_2$ with $H_2$ for these discharges. The calculated excitation by $H^+$, $H^+_1$ and $H^+_3$ ions is generally less important, although the model results for ions are less certain because of the absence of low-energy excitation cross-sections. The predictions of the role of $H^−$ ions show that, although the $H^−$ can lead to $H(n = 3)$ with energies higher than expected from the applied voltage, the experiments analyzed showed no convincing evidence for such fast excited atoms. The direct demonstrations of linearity of the magnitude of the $H_n$ emission at low $H_2$ pressures over current density segments of up to four orders of magnitude and the applicability of a model linear in current density over eight orders of magnitude in current density is an important result of this paper. The test is consistent with the basic assumption of the model that the kinetics of these discharges includes a sequence of collisions of active species, i.e. ions, atoms and molecules in ground or excited states, with the undissociated hydrogen gas. This test shows that collisions between two or more particles created by the discharge are of little importance. Therefore, this result should put to rest claims by Mills, Phillips and coworkers [61, 62] that the ‘excessively broadened’ $H_n$ emission from their dc discharges is a result of energy made available by collision of a dissociation product, e.g., an $H$ atom and another excited atom or dissociation product.

The cross-section set and surface-interaction probabilities for hydrogenic species have been extended to include the production and loss of $H^+$ and more accurate representations of published backscattered $H$ atom, $H^+$ ion, and $H(n = 3)$ atom fluxes. Excitation of $H_n$ and negative ion formation probabilities at surfaces are very difficult to characterize and are currently based on very limited data. The simplified model of this paper still treats the angular distributions of the $H(n = 3)$ atoms as an adjustable parameter. The differential scattering data needed to overcome this deficiency includes extensive sets of differential cross-sections for the numerous processes considered so as to improve on published models using very
much simplified sets [7]. Cross-sections for excitation of the Balmer series and UV in H$_n^+$, H$^-$ and H$_2$ collisions with H$_2$ (and H atoms) at energies below 2 keV are particularly important and, except for H + H$_2$, are currently only educated guesses. Total rates of energy loss at energies below 10 keV by these species in H$_2$ are poorly known.

The different observable quantities discussed in this paper provide a range of approaches to learning about the transport and reactions of the hydrogenic particles in hydrogen discharges and plasmas. The H$_n$ Doppler profiles are a measure of the velocity distributions of not only the excited atoms, but of the ions, atoms and molecules that produced them. The spatial distributions of H$_n$ emission have proved to be a sensitive technique for demonstrating the importance of processes such as the reflection of fast H atoms from surfaces. Positive-ion-energy distributions are expected to be useful measures of the dominate process for energy gain by heavy particles from the electric field, although there are presently serious discrepancies between the model and experiment. The negative ion-energy distributions are a potentially valuable diagnostic for probing the electric-field distribution in various hydrogen discharges. From the atomic physics point of view, the wings of transverse H$_n$ profiles provide a measure of the angular distribution of H(n = 3) atoms, e.g., near a surface where the angular distribution of H(n = 3) atoms is usually dominated by diffuse atom emission. The low electron densities near the cathode result in an increasing contribution of wings relative to core in the negative glow and offer the possibility of study of the small wavelength shifts caused by heavy particles during target species excitation.

It is important to the future application of the kinetics model of this review that sets of differential cross-sections be developed for the dominant processes. These processes include elastic scattering, including symmetric charge transfer; inelastic processes, such as vibrational excitation and Lyman series excitation and ionization; and ion–molecule reactions, including ion and proton transfer. Although the present hydrogen kinetics model has been applied only to H$_n$ production in the various moderate-current discharges of this paper, the kinetics model is readily extended to the production of Lyman lines and the near UV continuum.

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Note added in proof. Subsequent to the submission of this review and in direct conflict with our analyses and conclusions, Louriero and Amorim [67] have proposed that the Doppler-broadening experiments analyzed in sections 4 and 5 have been misinterpreted and that the wings of the H$_n$ profiles do not show the presence of excited H(n = 3) atoms with kinetic energies in the 10 to 100 eV range. Several assumptions of this proposal make their arguments invalid for these measurements of ‘excess’ Doppler broadening. These authors’ assumption of an isotropic velocity distribution is inconsistent with the highly anisotropic Doppler profiles observed along the discharge axis in many experiments [1, 2, 8, 10, 12, 40, 56]. The differences between the authors’ calculated line shapes and the Gaussians customarily fitted to the observed profiles over a wide range of spectral intensities cannot lead to the proposed order of magnitude errors in the mean energies (or corresponding ‘temperatures’) inferred for the excited H atoms. These authors’ assumption that the proton transfer reaction of H$_2^+$ with H$_2$ to form H$_3^+$ results in measurable emission from mono-energetic H(n = 3) atoms at energies sufficient to explain the H$_n$ profiles is inconsistent with the observations that the reaction occurs with significant probability only for laboratory energies below about 10 eV [68], does not produce electronic excitation [69], and that the exothermic energy is broadly distributed among levels of the product H$_3^+$ [70, 71] and, therefore, among the kinetic energies of the product H atoms.

Appendix A. H$^-$ properties

Figure 15(a) shows recommended cross-sections for collisions of H$^-$ with H$_2$. The cross-sections for momentum-transfer collisions and for electron detachment are the same as in [30],

![Figure 15](https://example.com/figure15.png)

Figure 15. (a) Cross-sections for collisions of H$^-$ with H$_2$. (b) Cross-sections for H$^-$ production.
except that these and other cross-sections have been extended to 100 keV using data from [72]. Of particular interest is the cross-section for the production of $H(n = 3)$ in collisions of $H^-$ with $H_2$ shown by the dashed curve of figure 15(a). This cross-section is based on the measurements of Geddes et al [39] at energies from 5 to 25 keV. At the very important lower energies, it is scaled from the proposed cross-section for $H_2$ excitation by $H^+$ from [1]. This long extrapolation leads to considerable uncertainty in the predicted $H_2$ excitation by $H^-$ in section 5.1. Obviously, there is a need for direct measurements of this process at lower energies.

Figure 15(b) shows cross-sections for $H^+$ production used in the model of $H_2$ discharges in this paper. The projectiles and the associated references utilized are $H$ [72–74], $H_2$ [75], $H^+$ [72, 76, 77], $H_2^+$ [78, 79], and $H_3^+$ [78, 79]. Note that the cross-sections for $H^+$ formation in collisions of $H$ atoms with $H_2$ from Van Zyl et al [73] are significantly larger, particularly at low energies, than those for $H^+$ formation in collisions of $H_2^+$ [72] and $H_2$ [75] with $H_2$. The present model interprets the literature as showing that for all projectiles the $H^+$ production used in section 5.1.

The predictions of this expression (smooth curves) for $H^+$ in Ni show agreement with Monte Carlo calculations for $D^+$ incident on Ni shown by the points in figure 16(a). Note the close equality of backscattering expected for $H^+$ and $D^+$ [37]. The empirical expression also agrees well with the Monte Carlo predictions of Oen and Robinson [85]. The agreement with the experiments of Aratari and Eckstein [86] is only fair. As a check on the empirical expression, the numerical integrations of (C.1) are compared with the ‘particle reflection coefficient’ $R_N$ data in figure 16(b). There is good agreement with the empirical fit to the published $R_N$ data discussed in [1].
Figure 16. (a) Energy distribution for backscattered D atoms from nickel bombarded with D⁺. The points are scaled from the Monte Carlo calculations of Eckstein and Verbeek [37]. The curves are the present empirical fits to these data. (b) Backscattered fractions obtained from the integration of empirical (curve) and Monte Carlo (points) energy distributions for protons on nickel [38].

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