Tests of Features of Field-Acceleration Models for the Extraordinary Selective H Balmer α Broadening in Certain Hydrogen Mixed Plasmas

R. Mills, K. Akhtar

BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ 08512

The validity of field-acceleration models to explain selective broadening in hydrogen-mixed plasmas was investigated by mapping the width of the emitted 656.3 nm Balmer α line from glow discharge Ar/H_2 (95/5%) as well as He/H_2 (95/5%) plasmas as a function of gas pressure and field strength using a cell with needle-like electrodes (fine-tip tungsten electrodes of 3 mm diameter). To explain the symmetrical (Gaussian) peak shape of selective, extraordinary broadening of the hydrogen Balmer lines, field-acceleration mechanisms require a "reflector" to reverse the momentum of positive ions gained from the electric field to give rise to fast H going away from the cathode in the same abundance as that moving towards the cathode. Not only does the reflector have to have a production efficiency of unity in the reverse-electric-field direction, but to be consistent with observations, a "divertor" must also exist such that the ratio of fast H of any given energy towards and away from the cathode remains equal while the equal ratio is also formed in all directions including the direction perpendicular to the field. The existence of an ideal reflector was tested by elimination of the possible candidates, the plane cathode or gas matrix, proposed in the latest versions of field-acceleration models by using needle electrodes and by decreasing the plasma-gas pressure by over an order of magnitude, respectively. No effect on the symmetrical broadening was observed. Furthermore, field-acceleration models require that the broadening is predominant in the cathode fall region along the direction of the strong field and is essentially zero everywhere except where the high voltage drop occurs. But, the broadening was mapped throughout the cell and no position effect was observed including perpendicular to the field and in regions far from the high-field regions. The field dependence was directly tested by varying the applied voltages, and again no effect was observed over the applied-voltage range of 475-620 V. Moreover, in former reports, the feature of the requirement of a divertor was ignored or argued not to exist despite data to the contrary showing that the broadening was independent of angle with respect to the field. Inescapable failings of all field-acceleration models are that the broadening was the same parallel as it was perpendicular to the field, and this broadening was undiminished even in regions where there was no high field. An energetic chemical reaction of hydrogen as the source of broadening explains the isotropic effect, the selective H broadening, the lack of a requirement for a divertor or reflector, the new feature reported by the authors of time dependence, lack of an applied-field dependence, and the observation that only particular hydrogen-mixed plasmas show the extraordinary broadening.

Key Words: DC plasma, He/H_2 and Ar/H_2 plasmas, excessive line broadening, resonant energy transfer mechanism, field-acceleration mechanism, mapping, role of reflector and divertor, pressure and field dependence

I. INTRODUCTION

Plasmas from sources such as glow, RF, and microwave discharges that are ubiquitous in diverse applications ranging from light sources to material processing are now increasingly becoming the focus of a debate over the explanation of the results of ion-energy-characterization studies on specific hydrogen "mixed gas" plasmas. In mixtures of argon and hydrogen, the hydrogen emission lines are significantly broader than any argon line. Historically, Kuraica and Konjevic [1-2], Videnovic et al. [3], and others [4-10] have characterized mixed hydrogen-argon plasmas by determining the excited hydrogen atom energies from measurements of the line broadening of one or more of the Balmer α, β, and γ lines of atomic hydrogen at 656.28, 486.13, and 434.05 nm, respectively. They found that the Balmer lines were extremely broadened and explained the phenomenon in terms of Doppler broadening due to the various models involving acceleration of charges such as H^+, H_2^+, and H_3^+ in the high fields (e. g. over $10\ kV/cm$) present in the cathode fall region herein called field-acceleration models (FAM). The field-acceleration mechanism which is directional, position dependent, and is not selective of any particular ion cannot explain the Gaussian Doppler distribution, position independence of the fast H energy, absence of the broadening of the molecular hydrogen and argon lines, gas composition dependence of the hydrogen mixed plasma, and are often not internally consistent or consistent with measured densities and cross sections.

For example, Djurovic and Roberts [5] recorded the spectral and spatial profiles of Balmer α line emission from low-pressure RF (13.56 MHz) discharges in $H_2 + Ar$ mixtures in a direction normal to the electric field. The introduction of Ar in a pure H_2 plasma increased the number of fast neutral atoms as evidenced by the intensity of the broad component of a two-component Doppler-broadened Balmer α line profile. Independent of cell position or direction, the average energy of a wide profile component was 23.8 eV for voltages above 100 V, and the average energy of a slow component was 0.22 eV. The mechanism proposed by Djurovic and Roberts is the production of fast H atoms from electric field accelerated H_2^+. The explanation of the role of Ar in the production of a large number of excited hydrogen atoms in the $n=3$ state, as well as raising their energy for a given pressure and applied RF voltage, is that collisions with Ar in the plasma sheath region enhances the production of fast H_2 from accelerated H_2^+. The fast H_2 then undergoes dissociation to form fast H that may then be excited locally to the $n=3$ state by a further collision with Ar. The local excitation is a requirement since the atomic lifetime of the hydrogen $n=3$ state is approximately $10^{-8}\ s$, and the average velocity of the hydrogen atoms is $<10^5$ m/s. Thus, the distance traveled must be less that 0.001 m. A problem with this mechanism is that H_2^+ is insufficiently low as measured by Radovanov et al. [7], and they concluded that H_3^+ rather than H_2^+ was the primary source of fast H emitted from the surface of the powered electrode.

Thus, mapping of the inter-electrode region by Djurovic and Roberts [5] and also Radovanov et al. [6] revealed a surprising result that the "hot" H of 23.8 eV was independent of position or direction over a wide range of gas pressures, applied RF voltages, and hydrogen concentration in Ar/H_2 mixtures. This presents a significant problem for field-acceleration models. Since the field is directional, the fast-H energy is predicted to be highest along the direction of the field with the greatest intensity in the cathode fall region. Moreover, rapid thermalization should confine the fast H to the location at which it was formed. Thus, no significant broadening should occur outside of the cathode-fall region. Counter to expectations, it was observed unchanged throughout the interelectrode region. Even more problematic for FAM is the recent results extending the line-width mapping outside of the interelectrode region [11-15]. Undiminished excessive broadening beyond the interelectrode region has been confirmed by a number of recent experiments. For example, low pressure (0.5 Torr) capacitively-coupled RF He/H_2 (95/5%) as well as Ar/H_2 (95/5%) plasmas showed excess broadening throughout the volume (13.5 cm ID x 38 cm length) of a GEC-type cell; not merely in the vicinity of the electrodes of Ar/H_2 plasmas as reported by several groups. About 50% of the hydrogen of the He/H_2 was "hot" with an average hydrogen atom energy of 40-50 eV, and Ar/H_2 showed a single fast or "hot" 40-50 eV population. The broadening was undiminished at 15 cm from the powered electrode, independent of power over a substantial range, but dependent on the hydrogen concentration. In contrast to the atomic hydrogen lines, no broadening was observed in helium or argon lines. Also, in "control" Xe/H_2 plasmas run in the same cell at similar pressures and absorbed power, no significant broadening of atomic hydrogen, Xe, or any other lines was observed. These experiments have been repeated and extended to other mixed hydrogen plasmas including hydrogen alone and water vapor plasmas [11, 13-15]. Another feature of these results is that the broadening was found to be time dependent that is indicative of an energetic chemical reaction rather than simple field acceleration [11, 13-14].

From the width of the emitted 656.3 nm Balmer α line, it was found that hydrogen and water-vapor capacitively-coupled RF plasmas showed excess broadening throughout the volume (13.5 cm ID x 38 cm length) of a GEC-type cell; not merely in the vicinity of the electrodes of hydrogen and Ar/H_2 plasmas as reported by several groups [11]. Two populations were observed—a typical slow population of <1 eV that was independent of time, and a new phenomenon, an extraordinary fast population that increased from zero to a significant portion of the Balmer α emission with time, was also observed under no-flow conditions. The peak width and energy also increased with time up to a 0.7 nm half-width corresponding to an average hydrogen atom energy of 200 eV. The broadening was undiminished at 15 cm from the powered electrode, independent of power and electric field over a substantial range. In contrast to the atomic hydrogen lines, no broadening was observed in oxygen lines. Also, in “control” Xe/H_2 plasmas run in the same cell at similar pressures and absorbed power and electric field, no significant broadening of atomic hydrogen, Xe, or any other lines was observed.

With the observation that the H energy in the negative glow is higher than that in the cathode fall region Videnovic et al. [3] also encountered this problem of broadening in regions that were inexplicable using FAM. Then, they proposed a new model wherein fast neutrals are additionally excited by collisions with electrons. Yet, the electron temperature T_e in these plasmas is only about 1 eV [16]; whereas, the H atom temperature T_H in terms of its energy in the negative glow region was about 50 eV. Since $T_H >>> T_e$ the energetic atoms would be expected to transfer energy to the electrons during a collision rather than the reverse process as proposed by Videnovic et al. [3]. Moreover, the results of the Langmuir probe measurements for the electron density n_e for the capacitively coupled RF, glow discharge, inductively coupled RF, and microwave plasma cells that showed selective, excessive fast H were 10^{10}-10^{11} cm^{-3} [6-7], 10^{9}-10^{11} cm^{-3} [1], 10^{9} cm^{-3} [17], and $<10^{9}$ cm^{-3} [16], respectively. The hot H density in all cases measured by Mills et al. [16] was typically two orders of magnitude higher that the electron density which further eliminates hot electrons as the source of hot H in regions of low field.

Other proponents of the FAM such as Cvetanovic et al. [18] have begun to address the fact that the H is fast beyond regions where field-acceleration can be the source and have also resorted to the use of the two separate models for different regions of the plasma—FAM in the cathode fall region and electron heating outside this region. Cvetanovic et al. [18] propose that high-energy electrons in the negative glow region are the source of excessive broadening here. In the same paper, they contradict their explanation with the statement that there is a “large contribution of fast excited hydrogen atoms having more than two orders of magnitude larger energies (see Fig. 4), than the electron temperature, which is of the order of 0.5 eV”. They make this and a number of other incorrect statements and misrepresentations of the data as arguments against an alternative resonance transfer model (RTM) when in fact their data directly supports the RTM that is based on a newly discovered chemical reaction of atomic hydrogen involving a resonant energy transfer.

The corresponding newly discovered plasma source also shows broadening as further invalidation of the FAM. Plasmas of certain catalysts that provide a net enthalpy equal to an integer multiple of the potential energy of atomic hydrogen $m \cdot 27.2\ eV$, such as Sr^+ and Ar^+ mixed with hydrogen produced strong EUV and visible emission [19-34]. These hydrogen plasmas called resonant transfer- or rt-plasmas were observed to form at low temperatures (e.g. $\approx 10^3\ K$) and an extraordinary low field strength of about 1-2 V/cm when argon and strontium were present with atomic hydrogen. The hydrogen kinetic energy determined from the H Balmer

α line increased from an initial 1 eV to an extraordinarily fast 25 eV over a six-hour period [23-30, 33-34]. The spectroscopic [19-38], thermal [20, 26-27, 36, 39-40], and chemical data [19-20, 26-27, 29, 41-43] reported previously support the possibility that a novel catalytic reaction of atomic hydrogen to form more stable hydrides exists and may power a new light and laser source [19-28, 31-34, 38, 46] and be the source of fast H [23-30, 33-34]. Furthermore, He^+ fulfills the catalyst criterion—a chemical or physical process with an enthalpy change equal to an integer multiple of $27.2\ eV$ since it ionizes at $54.417\ eV$ which is $2 \cdot 27.2\ eV$. Ar^+ may also serve as a catalyst since its ionization energy is about $27.2\ eV$. Thus, the resonance transfer mechanism is also a candidate to explain the broadening in RF and glow discharges wherein a catalyst is present with atomic hydrogen [11-16].

The RTM predicts excessive broadening due to a novel energetic chemical reaction of H involving a two-step energy transfer—a first resonant energy transfer from H to a catalyst and then a second radiative emission or a resonant kinetic energy transfer to another H that serves as a third body to take away the remaining reaction energy as given previously [13, 19]. The first energy transfer has been confirmed by the observation of the characteristic highly ionized states of the catalyst [24-34]. The radiative emission has been confirmed by novel VUV emission [19, 35-37], and the third-body energy transfer has been confirmed by the observation of highly energetic H from many plasma sources that cannot be explained by FAM [11-16, 33-34, 35-36, 44-46].

In recent spectroscopy studies [19], atomic catalytic systems involving helium ions and two H atoms were used. In the latter case, the potential energy of atomic hydrogen is $27.2\ eV$ such that two H atoms formed from H_2 by collision with a third, hot H can also act as a catalyst of $54.4\ eV$ for this third H to cause the same transition as He^+ as the catalyst. The energy transfer is predicted to pump the He^+ ion energy levels and increase the electron excitation temperature of H in helium-hydrogen and hydrogen plasmas, respectively. Following the energy transfer to the catalyst the radius of the H atom is predicted to decrease as the electron undergoes radial acceleration to a stable state having a radius that is 1/3 the radius of the uncatalyzed hydrogen atom with the further release of $54.4\ eV$ of energy. This energy may be emitted as a characteristic EUV continuum with a cutoff at 22.8 nm and extending to longer wavelengths, or as third-body kinetic energy wherein a resonant kinetic-energy transfer to form fast H occurs. Subsequent excitation of these fast $H(n=1)$ atoms by collisions with the background species followed by emission of the corresponding $H(n=3)$ fast atoms is predicted to give rise to broadened Balmer α emission. The product $H(1/3)$ reacts rapidly to form $H(1/4)$, then molecular hydrino, $H_2(1/4)$, as a preferred state. Extreme ultraviolet (EUV) spectroscopy and high-resolution visible spectroscopy were recorded on microwave and glow and pulsed discharges of helium with hydrogen and hydrogen alone. Pumping of the He^+ ion lines occurred with the addition of hydrogen, and the excitation temperature of hydrogen plasmas under certain conditions was very high. Furthermore, for both plasmas providing catalysts He^+ and $2H$, respectively, the EUV continuum and extraordinary (>50 eV) Balmer α line broadening were observed. $H_2\left(1/4\right)$ was observed by solution NMR at 1.25 ppm on gases collected from helium-hydrogen and water-vapor-assisted hydrogen plasmas and dissolved in $CDCl_3$.

Furthermore, it was observed that the energy released to produce hydrogen states such as $H\left(1/4\right)$ gives rise to broadening of H that is nondirectional, position independent, selective to H, Gaussian Doppler, often two orders of magnitude in excess of the electron temperature, and specific to plasmas with atomic hydrogen and a catalyst. Such plasmas include hydrogen mixed with argon [12-13, 16, 45], helium [11, 16, 19, 44], potassium [29-30, 33-34], Rb(II) ions [29-30, 33-34] or Sr(II) ions [23-28], water vapor plasmas [11, 15, 46], and pure hydrogen plasmas [13-14]. All aspects of the failings of FAM can be explained by the RTM as well as other results such as broadening reported in rt-plasmas [26-30, 33-34] and microwave driven plasmas [16, 44-46] where there is no high electric field in a cathode fall region $(>1kV/cm)$ to accelerate positive ions [1-10, 18].

With the consideration of another physics aspect of the observation of hot H plasmas by Balmer-line broadening measurements, all of the points of Cvetanovic et al. [18] against RTM actually support it. Plasma modeling at ~1 Torr demonstrates that the lifetime for excitation to the Balmer α state with an electron temperature of 1 eV is on the order of 1 ms which is long compared to the thermalization lifetime of fast H of 5 μs. In the case that the electron temperature is 10 eV, the excitation lifetime decreases markedly to 1 μs. The electron energies and densities decrease from the cathode fall region. Thus, the excitation of fast H and therefore the intensity is anticipated to decrease, but not necessarily the energy of fast H itself[1]. This is a function of the catalysis rate based on the reaction first at the cathode, then later in bulk of the plasma as discussed previously [13]. The weak dependence of the fast H energy of ~60 eV and the decrease in intensity from the cathode fall region is predicted by the RTM and confirmed by the Cvetanovic et al. [18][2]. The broadening is also observed perpendicularly to the field essentially undiminished in energy in contradiction to the FAM and the analysis of Cvetanovic et al. [18]. Measurements on pure hydrogen RF-discharge plasmas in a GEC-type cell by Phillips

---

[1] The low energies and absence of the potential for a small high energy population, combined with low densities are detrimental factors for observing fast H present in certain hydrogen mixed microwave plasmas. Alternative methods are measurement of the widths of the EPR (electron paramagnetic resonance) peak or hyperfine line.

[2] In Figures 4a and b of Cvetanovic et al., the side-on recorded fast-H energies at z=2.5 mm and z=4.5 mm are given as 62 eV and 55 eV, respectively. There is no energy given for the enlarged Figure 4c which shows the end-on line. But measurements by hand indicate that the fast H energy of about 70 eV is similar to that in the other figures.

et al. [13] further support the RTM on these aspects. Time-dependent excessive broadening of the Balmer lines was found to exist throughout the plasma, and not just in the region between the electrodes, and the effect was independent of direction of the electric field. As expected, based on the electron densities and energies, the intensity was greatest in between the parallel-plate electrodes; however, the highest energy was 15 cm from the electrodes where the field is essentially zero. This cannot be explained by the FAM, but is consistent with the RTM.

The high electric field in RF and glow discharge plasmas is essentially confined to the cathode fall region which is typically no more than a few mm from the cathode [6] in contrast to the reported previously broadening that was independent of position up to 15 cm from the cathode [11-15], and only the atomic hydrogen lines are broadened [1, 3, 7, 11-16, 44, 47-50]. Since direct mapping of the broadening outside of the inter-electrode region is a rigid test of the catalytic energy-transfer mechanism versus models based on field acceleration, this was performed. In this study, the broadening was mapped throughout the cell and no position effect was observed as required by field-acceleration models. Based on conservation of energy and momentum gained from the directional electric field, FAM predict that there should be no broadening observable in the direction perpendicular to the electric field [18]. Thus, other serious failures of this model were that the broadening was the same parallel as it was perpendicular to the field [13-14, 18], and this nondirectional broadening was undiminished even in regions where there was no high field [11-15]. The field dependence was then directly tested by varying the applied voltages, and again no effect was observed over the applied-voltage range of 475-620 V in contradiction to expectations based on FAM. Even more surprising was the observation that the peak shape was Gaussian independent of direction and position with respect to the electric field [13-14, 15]. Thus, to explain the data, FAM require an ideal reflector to explain the symmetrical peak shape and an ideal divertor to explain the nondirectionality of the broadening. The nature of these aspects can be deduced from the physics of any broadening where the energy is provided by a unidirectional electric field.

Since the broadening is unchallenged as Doppler broadening [1-7] corresponding to high atomic kinetic energies, a mechanism must exist to impart velocity to hydrogen atoms. In FAM, the velocity and corresponding kinetic energy of hot H is acquired by accelerating an ion in one direction due to the unidirectional nature of the applied field. Then, the fast ions or ions must give rise to fast H in a manner consistent with all of the data. Initial models proposed the acceleration of H_2^+. This was modified to H_3^+ as the accelerated ion when it was determined that the H_2^+ concentration was insignificant, and H_3^+ was the dominant ion [7]. Since the electric field is conservative, the symmetry of the broadened profile cannot be explained simply by the acceleration of the initially proposed H_2^+, H_3^+, or any positive ion towards the cathode as such a mechanism could only account for the red portion of the profile with the line of sight towards the cathode. A mechanism for the production of the blue portion that is symmetrical with the red portion is required. Such a mechanism was not suggested other than reflection of accelerated ions from the cathode [1-7]. Based on inference from a mechanism involving gas matrix interactions [3], a modification is to consider reflection from the plasma gas itself.

Since the measurements were taken perpendicular to the applied electric field [1-7] as well as parallel [13, 18], the symmetrical Doppler shape of both components centered at the same wavelength indicated that there were no directional velocity effects from the applied electric field [13]. This would not be expected since the red and blue parts of the wings due to fast H must come from at least two different mechanisms. The red wing due to fast atoms moving toward the powered electrode arises from accelerated H_2^+ or H_3^+; whereas, H atoms moving away from the electrode arise from back scattered fast H atoms or fast H atoms formed on the electrode from decomposition of fast H_2^+, H_3^+, or fast H_2. Momentum transfer must occur at the electrode, and gaps and/or asymmetries in the intensity would be expected for any proposed mechanism. A Maxwellian distribution would not be anticipated from these different mechanisms; thus, a Gaussian line shape would not be anticipated. Rather a single source of fast H formed independent of direction is needed.

The requirement of an ideal reflector and divertor defined as a source of the momentum reversal of the field-accelerated ions, which gives rise to the nondirectional symmetrical Gaussian-peak shape in mixed hydrogen plasmas, was tested by elimination of the reflector. The cathode reflector/divertor was eliminated by replacing the typical plane electrode with a needle-like electrode. The gas reflector/divertor was eliminated by testing the peak shape as function of lowered gas pressure over an order of magnitude range that corresponded to lower cross sections for reflection. The peak shape was determined parallel and perpendicular to the electric field directions. If the fast H is due to field acceleration of positive ions and reflection accounts for the blue wing, then a directional effect and dependence on the cross section of the reflector must exist. No such effect was observed. The broadening was found to be absolutely symmetrical, independent of the direction of observation relative to the field even with needle-like electrodes and over the entire range of pressures studied even down to less than 1/10 the pressure typically reported in mixed-hydrogen plasmas. Given that field lines end perpendicularly to a conductor, a needle in this case, the FAM is untenable in the face of these results.

Lastly, the dependence of the excessive broadening on the plasma gas was considered. Kuraica and Konjevic [1] observed 50 eV anomalous thermal broadening of the Balmer lines during plane-cathode abnormal glow discharges of hydrogen-argon mixtures that was not observed with neon-hydrogen mixtures or pure hydrogen irrespective of cathode material, copper, carbon, or silver. To explain the excessive broadening with the presence of argon, they have proposed the quasiresonant charge-transfer process

$$Ar^{+(m)} + H_2 \to Ar + H_2^+ \qquad (1)$$

with the further reaction

$$H_2^+ + H_2 \to H_3^+ + H \qquad (2)$$

occurring to a significant extent due to its large cross section. The H_2^+ or H_3^+ ion must gain energy in the electric field of the discharge before dissociation. Otherwise, the large energy of excited hydrogen atoms (on the average 50 eV per atom) cannot be explained.

The broadening in argon-hydrogen plasmas cannot be explained purely by a resonant energy transfer to H_2^+ which is accelerated in the electric field to dissociate as energetic atomic hydrogen as proposed by Kuraica and Konjevic [1] or the excitation of matrix gases by collisions with accelerated H_2^+ [3]. This is based on the fact that since the electric field is conservative, the symmetry of the broadened profile cannot be explained simply by the acceleration of H_2^+ or any positive ion towards the cathode as such a mechanism could only account for the red portion of the profile with the line of sight towards the cathode. A mechanism for the production of the blue portion that is symmetrical with the red portion is required. Such a mechanism was not suggested. This mechanism was also eliminated based on mass-resolved measurements on ion abundance and ion kinetic energy [7] that showed that the amount and energies of H_2^+ was grossly insufficient to account for the hot H.

Videnovic et al. [3] explain the argon effect as due to the more efficient production of H_3^+. However, the most abundant ion in a pure hydrogen plasma is also H_3^+ [51], and the H_3^+ explanation was eliminated based on known cross sections in these plasmas for its production and destruction [16, 44]. Furthermore, Videnovic et al. ignored other processes that could diminish the acceleration of hydrogen ions in the cathode fall region. For example, the dissociative recombination cross section for H_3^+ given by

$$e^- + H_3^+ \to H_2 + H \qquad (3)$$

is $10^{-14}\ cm^2$ [52], about an order of magnitude greater than the cross sections of the dominant reactions which may give rise to H_3^+ [16, 44]. Thus, except where the electron density may be sufficiently low [3], it is not apparent that H_3^+ could give rise to fast H even if it was produced in greater amounts with the addition of argon.

Videnovic et al. [3] propose that the absence of line broadening with argon alone is explained by a large cross section for charge-exchange that prevents the acceleration of argon ions to high energies. For example, the charge-exchange reaction

$$\left(Ar^+\right)_f + Ar_s \to Ar_f + \left(Ar^+\right)_s \qquad (4)$$

(s designates slow, and f designates fast) has a cross section of the order of $10^{-15}\ cm^2$, in the energy range 10-1000 eV. This cross section is about a factor of 30 times that for charge-exchange processes involving H_3^+ and H^+; thus, Videnovic et al. [3] argue that the diminished collisions result in higher energy ions reaching the cathode in the case of H_3^+ and H^+ compared to Ar^+. But, the cross section for Ar^+ is still very small corresponding to a mean free path at 30 mTorr pressure of about the width of the cathode fall region of 0.1-0.2 cm given by Videnovic et al. [3].

Similarly, their argument that argon gas is more transparent for back scattered fast H atoms than hydrogen gas is not persuasive. They calculate that 66% of reflected H atoms arrive at the negative glow region without collisions in the former case and 18% in the latter case at similar gas pressure and temperature ($T_g\left(Ar/H_2\right)=T_g\left(H_2\right)=1000\ K$, $P\left(Ar/H_2\right)=320\ Pa$, and $P\left(H_2\right)=228\ Pa$). However, they assumed a cathode fall region that was twice the length in the hydrogen case ($L=0.158\ cm$ versus $0.085\ cm$), and even if this factor of two difference existed, it could be more than compensated by reducing the hydrogen pressure to one half that of the argon-hydrogen plasma. In fact, intense excessive broadening is not observed in hydrogen with $P\left(H_2\right)=150\ Pa$ [1]; whereas, it is in the case with $P\left(Ar/H_2\right)=320\ Pa$.

Another argument against the greater transparency of argon is that although the intensity is much smaller, excessive broadening is observed at the cathode fall region for hydrogen alone which is greater (125 eV) than that observed in the case of an argon-hydrogen mixture (95 eV) [1].

A further internal inconsistency arises from the explanation of the argon effect by Radovanov et al. [6] compared to that of Videnovic et al. [3]. Radovanov et al. [6] conclude that in the sheath, the Doppler-shifted emission cannot be due primarily to electron collisions with fast H atoms, since calculations show that the electron density on the sheath region should be low. Rather, the emission from the fast H atoms stems from energetic ions or atoms formed near or at the powered electrode, and then are able to travel into the discharge volume before being collisionally excited to the n=3 state. The increase in Doppler-shifted Balmer α emission when argon is added to H_2 is attributed to the high excitation cross section of fast H atoms. Thus, argon provides a collisionless environment according to Videnovic et al. [3] that allow ions to accelerate and fast H to propagate; yet, it is highly collisional according to Radovanov et al. [6] in order to form the excited n=3 atoms. This explanation is even less plausible given observations that the similar broadening was observed with helium-hydrogen as with argon-hydrogen [12-14, 16, 44-45] even though the masses of the noble gasses are very different, but no broadening was observed with neon [1, 50] or xenon with hydrogen [12-16, 44].

The data is consistent with the RTM wherein specific species such as $2H$, Sr^+, He^+, and Ar^+ act catalytically through a resonant energy transfer mechanism to create "hot" hydrogen atoms in plasmas. Furthermore, as discussed *infra.* in FAM, Ar uniquely forms H_2^+ or H_3^+ and is collisional or transparent depending on the field-acceleration model. Thus, helium is only predicted to cause broadening in the catalytic energy-transfer model. Thus, it was tested under identical conditions as for argon. The impact of applied power and hydrogen concentration were studied as well. The results were surprising in that a field-dependent mechanisms was not supported which reinforces previous results [11-16, 23-30, 33-34, 44-46]; whereas, an energetic chemical reaction of hydrogen as the source of broadening (i.e. the RTM) predicts the observations.

II. EXPERIMENTAL

The width of the 656.3 nm Balmer α line emitted from He/H_2 (95/5%), Ar/H_2 (95/5%), and Xe/H_2 (95/5%)-mixture plasmas was measured with a high resolution visible spectrometer capable of a resolution of $\pm 0.006\ nm$ over the spectral range 190-860 nm. The DC glow-discharge light source shown in Figure 1 comprised fine-tip, 2% thoriated tungsten electrodes of 3 mm diameter inside a 1.25 cm diameter quartz tube. The electrodes were spaced 2 cm apart except where indicated for the study of the line-width dependence on the applied electric field. Here, the spacing was adjusted to achieve the desired applied voltage. The very fine electrode tips that tapered to a point over the last inch were used primarily to minimize the surface area perpendicular to the axis of the electrodes so that ions accelerated along the electric-field lines could not bounce off of the surface in the reverse direction. This configuration greatly reduced the backscatter process that FAM use to explain the symmetry in the H_α broadening. High-resolution plasma emission spectroscopy was performed along the electric field lines (end-on) and perpendicular to the field lines (side-on). For side-on observation an axial scan of the plasma emission along the cathode rod was also obtained. The DC plasma setup was placed on an X-Y motion table to record an accurate axial measurement without changing the position of the fiber optic bundle. Here, the axial distance along the cathode is defined with the cathode tip located at z=0 cm as shown in Figure 1. In order to sample plasma emission looking towards the anode as well as the cathode for the end-on observation the polarity of the powered electrode was reversed.

The plasma chamber was evacuated using a scroll pump. Noble gas-hydrogen (95/5%) was introduced into the evacuated chamber using independent mass flow controllers (MKS). The discharge pressure was maintained in the range of 0.05 Torr to 2 Torr by controlling the flow and pumping rate. A stabilized DC power supply (0-0.5 A and 0-2000 V) was used to maintain the plasma. High-wattage current-limiting resistors of 200 Ω were used in series with the power supply and generator. Following break down, the glow discharge was maintained with cathode-anode voltages and currents in the ranges of 300-620 V and 10-100 mA, respectively, depending upon the gas pressure, gas flow, and discharge configuration.

The plasma emission was fiber-optically coupled to a Jobin Yvon Horiba 1250 M spectrometer described previously [16] through a high-quality UV (200-800 nm) fiber-optic bundle having a numerical aperture of 0.12 with 12° acceptance angle and an 220F matching fiber adapter. The spectrometer had a 1250 mm focal length with a 2400 g/mm grating and a stand-alone power supply of 995 volts. In some instances a high-quality scientific grade liquid nitrogen cooled CCD array with 16 bit ADC with 20 KHz and 1 MHz read out was also used. The specifications were a measured resolution of ± 0.008 nm with the entrance and exit slits set to 20 μm, an accuracy of ± 0.05 nm, and a repeatability of ± 0.005 nm.

The hydrogen atom Doppler energies were calculated from the width of the 656.3 nm Balmer α line emitted from the DC plasmas [53]. The half-width of the Doppler broadened emission profile was obtained using a multi-Gaussian curve fit utilizing the curve fitting software GRAMS from Jobin Yvon Horiba. Each Balmer α spectral line was fit using one or two Gaussian curves: one for the "cold" (<1 eV) hydrogen and the second for "hot" (>10 eV) hydrogen. The full half-width $\Delta\lambda_G$ of each Gaussian results from the Doppler ($\Delta\lambda_D$) and instrumental ($\Delta\lambda_I$) half-widths:

$$\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2} \tag{5}$$

$\Delta\lambda_I$ in our experiments was 0.008 nm. The temperature was calculated from the Doppler half-width using the formula:

$$\Delta\lambda_D = 7.16\ X\ 10^{-7}\lambda_0\left(\frac{T}{\mu}\right)^{1/2}\ \text{nm.} \tag{6}$$

where λ_0 is the line wavelength in nm, T is the temperature in K ($1\ eV = 11,605\ K$), and μ is the atomic mass number (=1 for atomic hydrogen). In each case, the error in the average Doppler half-width over 5 scans was about ±5% that was attributed predominately to fluctuations in the plasma. It should be noted that for high-density plasma $>10^{13}$/cc, Doppler broadening competes with Stark broadening. In addition, a contribution to the broadened profile may arise from the mass motion of the plasma. However, for these glow discharges where the plasma density is low ($<10^{11}$/cc), the contribution of Stark broadening to the line shape profile can be neglected without loss of accuracy

III. RESULTS AND DISCUSSION

The normalized emission profile of 656.3 nm Balmer α line recorded normal (side-on) to the applied electric field direction along the cathode with a high resolution ($\pm 0.006\,nm$) visible spectrometer on DC discharge plasmas of Ar/H_2 (95/5%), He/H_2 (95/5%), and Xe/H_2 (95/5%) at 400 V and 20 mA are shown in Figures 2, 3, and 4, respectively. Significant broadening was observed for Ar/H_2 and He/H_2, but not for Xe/H_2. The Balmer α line profiles of the Ar/H_2 and He/H_2 plasma emission each comprised two distinct Gaussian peaks, an inner, narrower peak corresponding to a slow component with an average hydrogen energy of <1 eV and an outer, broader peak corresponding to a fast component of 40-50 eV. The slow population is assigned to thermal excitation in the plasma and matches those reported previously [1-16, 44]. In contrast, only the slow component was observed for Xe/H_2. In each case, the single slow population corresponded to an average hydrogen atom energy of <1 eV. The fractional concentration of each component, slow and fast, of excited (n=3) H atoms was determined from the corresponding ratio of area under the narrow and broad Doppler profile to the total area under the emission profile, respectively. The fractional concentration of the excited (n=3) slow part obtained from the relative curve-fit areas is 20-25%, and that of the fast hydrogen component corresponds to 80-75 % indicating that the production of fast hydrogen atoms is substantial.

It is extraordinary that energy is transferred selectively to hydrogen atoms in admixed plasmas such that only the hydrogen lines are broadened. Fig. 5(a) shows the emission profile of pure argon plasma at 1 Torr with only trace hydrogen. The inset figure shows the H_α profile with an increase of the sampling time by a factor of 20. It this case, the excited fast H atoms with energies ~ 35 eV were recorded; whereas, no change in Doppler broadening was observed for the 696.5 nm Ar I line. This effect cannot be attributed to mass differences in the hot and cold species when the admixed gas is switched to helium. Since the mass ratio of He to atomic hydrogen is 4:1, it is expected from the FAM that a comparable energetic concentration of helium atoms (Doppler broadened profile) will be present, especially for highly collisional plasmas at higher gas pressures. The Doppler half-width of the 667.82 nm He I line can be accurately resolved by the high-resolution spectrometer with an instrumental half-width of only 0.006 nm. In 1 Torr helium plasma with trace hydrogen, the Doppler half-width shown in Fig. 5(b) is only 0.012 nm corresponding to an average He-atom thermal energy of 0.2 eV; whereas, the excited fast H atoms are observed with energies of about 38 eV. Thus, the absence of hot helium atoms in the admixed plasmas where the hydrogen atoms have 30-40 eV energies also contradicts the FAM because the atomic mass ratios are comparable (4:1).

Furthermore, the broadening was not dependent on the position in the cell as shown in Figures 6 and 7 for Ar/H_2 and He/H_2, respectively. The axial plots showed the temperature and the fractional population of excited (n=3) hot hydrogen atoms were essentially undiminished even at a distance of 8 cm away from the cathode tip where most of the potential falls. Thus, the excessive broadening is independent of the electric field. Furthermore, the broadening is the same in the direction perpendicular to the field as it is parallel to the field as shown by comparing the results of the side-on (Figures 2 and 6) versus end-on (Figure 8) scans for Ar/H_2. The same result is obtained in the case of He/H_2 as shown by comparing the results of the side-on (Figures 3 and 7) versus end-on (Figure 9) scans. As shown by Eq. (4) of Cvetanovic et al. [18] (where $\theta = 0$ is perpendicular to the direction of the applied field), FAM predict no broadening to be observed perpendicularly to the field based on conservation of energy and momentum of ions accelerated along the electric field lines. The position independence and isotropic nature of the excessive broadening are serious failures of FAM.

Cvetanovic et al. [18] have argued that the decrease in hot-H intensity moving away from the cathode-fall region as evidence against the RTM. But, the observation of Balmer α emission from hot H requires excitation to the n=3 state. Thus, a fall off in intensity is anticipated since the electron density and energy decreases from the cathode-fall region. The intensity can be arbitrarily increased by increasing these parameters with a higher plasma current. Thus, the results are exactly as predicted for the RTM: fast H that is independent of position and is isotropic.

To confirm the RTM over the FAM, the dependence of the broadening on the electric field was directly tested by varying the applied voltage across the electrodes. The 656.3 nm Balmer α line width of 1 Torr Ar/H_2 (95/5%) DC plasma discharges was recorded side-on at z=4 cm for an electrode gap of 4 cm. Figure 10 shows the average energies and populations of the two-component profile for 4.75 W (475 V; 10 mA), 16.8 W (560 V; 30 mA), and 24.8 W (620 V; 40 mA). The average fast-hydrogen atom energy of 31-32 eV did not change with applied voltage over the range 475 V to 620 V indicating that the broadening was not dependent on the electric field. This absence of an electric-field dependency was confirmed by the absence of broadening in Xe/H_2 plasmas and the absence of broadening of hydrogen molecular lines or noble atom or ion lines.

Also, another important feature that is found with Ar/H_2 [1-7, 12-14, 16, 44], He/H_2 [12, 14, 16, 19, 44], pure hydrogen [13, 16, 19, 18, 44], and water vapor plasmas [11, 15] reported previously, is that the H peak profile was symmetrical. Reflection of electric-field-accelerated ions is required to produce a symmetrical peak shape in FAM as stated by Cvetanovic et al. [18]:

> "The rest of the accelerated ions reach the cathode, where they neutralize, or neutralize and fragmentize, and as a result of all interactions with cathode, fast H atoms are directed back towards the anode."

Thus, the replacement of a plane cathode with a needle would result in an asymmetrical peaks shape. Only the red wing away from the optical probe toward the cathode would be predicted since there is no axial perpendicular surface to reverse the forward momentum of ions accelerated along the electric field. But, this result was not observed as shown in Figures 11 and 12. The normalized end-on emission spectra of 1 Torr Ar/H_2 (95/5%), He/H_2 (95/5%), and Xe/H_2 (95/5%) plasmas looking towards the cathode and the anode showed a symmetrical emission profile. Furthermore, the symmetrical profile could not be explained by a gas-matrix-collisional effect since no change occurred in the peak shape as the pressure was varied by a factor of 40 from 0.05 Torr to 2 Torr as shown in Figures 13 and 14. Typically collisional-effects are proportional to the gas pressure squared. The symmetrical peak shape of the fast population was not dependent on the gas pressure whether recorded side-on or end-on. These results further confirmed the isotropic and position independence of the excessive broadening against the predictions of FAM, but fully consistent with the RTM.

IV. CONCLUSION

The results of the 656.3 nm Balmer α line measurements, recorded as a function of position in the cell, direction relative to the electric field, strength of the electric field, and pressure from He/H_2 (95/5%) as well as Ar/H_2 (95/5%) DC glow-discharge plasmas with needle electrodes supports the conclusion that field-acceleration models are not valid to explain selective broadening in hydrogen-mixed plasmas. The reflector capabilities of the cathode that are necessary to explain the symmetrical profile in FAM was removed by using needle-like electrodes. The peak shape remained symmetrical. The role of the gas matrix as a reflector or divertor was disproved. The gas pressure was varied more than an order of magnitude. The nondirectional, isotropic peak shape remained the same. The broadening was observed throughout the cell and was independent of angle with respect to the field; thus, it did not depend on the field strength. This further failure of FAM was confirmed by directly varying the applied voltage and observing no effect on the broadening. The broadening was only observed for helium and argon mixed plasmas, but not for xenon. Selective, excessive H broadening with He/H_2 shown in this study and in other cell-types [12, 14, 16, 44] is not predicted with any FAM. However, a chemical reaction with energy release that produces broadening of H that is time dependent [11, 13, 26-28], nondirectional, position independent, selective to H, Gaussian Doppler, often two orders of magnitude in excess of the electron temperature, and specific to plasmas with atomic hydrogen and a catalyst (Ar^+ and He^+ in this study) including those formed chemically [23-34] explains the data in total. The RTM is supported by the data; whereas, the FAM is not.

REFERENCES

1. M. Kuraica, N. Konjevic, “Line shapes of atomic hydrogen in a plane-cathode abnormal glow discharge,” Physical Review A, Volume 46, No. 7, October (1992), pp. 4429-4432.
2. M. Kuraica, N. Konjevic, M. Platisa and D. Pantelic, *Spectrochimica Acta* Vol. 47, 1173 (1992).
3. I. R. Videnovic, N. Konjevic, M. M. Kuraica, “Spectroscopic investigations of a cathode fall region of the Grimm-type glow discharge,” Spectrochimica Acta, Part B, Vol. 51, (1996), pp. 1707-1731.
4. S. Alexiou, E. Leboucher-Dalimier, “Hydrogen Balmer-α in dense plasmas,” Phys, Rev. E, Vol. 60, No. 3, (1999), pp. 3436-3438.
5. S. Djurovic, J. R. Roberts, “Hydrogen Balmer alpha line shapes for hydrogen-argon mixtures in a low-pressure rf discharge,” J. Appl. Phys., Vol. 74, No. 11, (1993), pp. 6558-6565.
6. S. B. Radovanov, K. Dzierzega, J. R. Roberts, J. K. Olthoff, Time-resolved Balmer-alpha emission from fast hydrogen atoms in low pressure, radio-frequency discharges in hydrogen,” Appl. Phys. Lett., Vol. 66, No. 20, (1995), pp. 2637-2639.
7. S. B. Radovanov, J. K. Olthoff, R. J. Van Brunt, S. Djurovic, “Ion kinetic-energy distributions and Balmer-alpha (H_α) excitation in $Ar-H_2$ radio-frequency discharges,” J. Appl. Phys., Vol. 78, No. 2, (1995), pp. 746-757.
8. G. Baravian, Y. Chouan, A. Ricard, G. Sultan, J. Appl. Phys., Vol. 61, (1987), p. 5249.
9. E. L. Ayers and W. Benesch, Phys. Rev., Vol. A37, (1988), p. 194.
10. A. V. Phelps, J. Phys. Chem. Ref Data, Vol. 21, (1992), p. 883.
11. R. L. Mills, B. Dhandapani, K. Akhtar, “Excessive Balmer α Line Broadening of Water-Vapor Capacitively-Coupled RF Discharge Plasmas,” Int. J. Hydrogen Energy, Vol. 33, (2008), pp. 802-815.
12. R. Mills, P. Ray, B. Dhandapani, “Evidence of an Energy Transfer Reaction Between Atomic Hydrogen and Argon II or Helium II as the Source of Excessively Hot H Atoms in RF Plasmas,” Journal of Plasma Physics, (2006), Vol. 72, Issue 4, pp. 469-484.24.
13. J. Phillips, C-K Chen, K. Akhtar, B. Dhandapani, R. Mills, “Evidence of Catalytic Production of Hot Hydrogen in RF Generated Hydrogen/Argon Plasmas,” International Journal of Hydrogen Energy, Vol. 32(14), (2007), 3010-3025.
14. K. Akhtar, J. E. Scharer, R. Mills, “Substantial Doppler Broadening of Atomic-Hydrogen Lines in DC and Capacitively Coupled RF Plasmas,” submitted.
15. J. Phillips, C. K. Chen, R. Mills, “Evidence of Energetic Reactions Between Hydrogen and Oxygen Species in RF Generated H_2O Plasmas,” Int. J. Hydrogen Energy, Vol. 33 (2008),

pp. 2419-2432.

16. R. L. Mills, P. Ray, B. Dhandapani, J. He, "Comparison of Excessive Balmer α Line Broadening of Inductively and Capacitively Coupled RF, Microwave, and Glow Discharge Hydrogen Plasmas with Certain Catalysts," IEEE Transactions on Plasma Science, Vol. 31, No. (2003), pp. 338-355.
17. D. Barton, J. W. Bradley, D. A. Steele, and R. D. Short, "Investigating radio frequency plasmas used for the modification of polymer surfaces," J. Phys. Chem. B, Vol. 103, (1999), pp. 4423-4430.
18. N. Cvetanovic, M. M. Kuraica, N. Konjevic, "Excessive Balmer line broadening in a plane cathode abnormal glow discharge in hydrogen" Journal of Applied Physics. Vol. 97, (2005), pp. 33302-1 to 33302-8.
19. R. L. Mills, Y. Lu, K. Akhar, "Spectroscopic Observation of Helium-Ion- and Hydrogen-Catalyzed Hydrino Transitions," submitted.
20. R. L. Mills, G. Zhao, K. Akhar, R. Chang, J. He, Y. Lu, W. Good, G. Chu, "Commercializable Power Source from Forming New States of Hydrogen," in press.
21. R. Mills, J. Dong, Y. Lu, "Observation of Extreme Ultraviolet Hydrogen Emission from Incandescently Heated Hydrogen Gas with Certain Catalysts," Int. J. Hydrogen Energy, Vol. 25, (2000), pp. 919-943.
22. H. Conrads, R. Mills, Th. Wrubel, "Emission in the Deep Vacuum Ultraviolet from a Plasma Formed by Incandescently Heating Hydrogen Gas with Trace Amounts of Potassium Carbonate," Plasma Sources Science and Technology, Vol. 12, (3003), pp. 389-395.
23. R. Mills and M. Nansteel, P. Ray, "Argon-Hydrogen-Strontium Discharge Light Source," IEEE Transactions on Plasma Science, Vol. 30, No. 2, (2002), pp. 639-653.
24. R. Mills and M. Nansteel, P. Ray, "Bright Hydrogen-Light Source due to a Resonant Energy Transfer with Strontium and Argon Ions," New Journal of Physics, Vol. 4, (2002), pp. 70.1-70.28.
25. R. Mills, M. Nansteel, and P. Ray, "Excessively Bright Hydrogen-Strontium Plasma Light Source Due to Energy Resonance of Strontium with Hydrogen," J. of Plasma Physics, Vol. 69, (2003), pp. 131-158.
26. R. L. Mills, J. He, M. Nansteel, B. Dhandapani, "Catalysis of Atomic Hydrogen to New Hydrides as a New Power Source," International Journal of Global Energy Issues (IJGEI), Special Edition in Energy Systems, Vol. 28, Nos. 2/3 (2007), pp. 304-324.
27. R. Mills, J. He, Z. Chang, W. Good, Y. Lu, B. Dhandapani, "Catalysis of Atomic Hydrogen to Novel Hydrogen Species $H^-(1/4)$ and $H_2(1/4)$ as a New Power Source," Int. J. Hydrogen Energy, Vol. 32, No. 12, (2007), pp. 2573-2584.

28. R. L. Mills, M. Nansteel, J. He, B. Dhandapani, “Low-Voltage EUV and Visible Light Source Due to Catalysis of Atomic Hydrogen,” submitted.
29. R. Mills, P. Ray, B. Dhandapani, W. Good, P. Jansson, M. Nansteel, J. He, A. Voigt, “Spectroscopic and NMR Identification of Novel Hydride Ions in Fractional Quantum Energy States Formed by an Exothermic Reaction of Atomic Hydrogen with Certain Catalysts,” European Physical Journal-Applied Physics, Vol. 28, (2004), pp. 83-104.
30. R. L. Mills, P. Ray, “A Comprehensive Study of Spectra of the Bound-Free Hyperfine Levels of Novel Hydride Ion $H^{-}(1/2)$, Hydrogen, Nitrogen, and Air,” Int. J. Hydrogen Energy, Vol. 28, No. 8, (2003), pp. 825-871.
31. R. Mills, P. Ray, “Spectroscopic Identification of a Novel Catalytic Reaction of Potassium and Atomic Hydrogen and the Hydride Ion Product,” Int. J. Hydrogen Energy, Vol. 27, No. 2, (2002), pp. 183-192.
32. R. Mills, “Spectroscopic Identification of a Novel Catalytic Reaction of Atomic Hydrogen and the Hydride Ion Product,” Int. J. Hydrogen Energy, Vol. 26, No. 10, (2001), pp. 1041-1058.
33. R. Mills, P. Ray, R. M. Mayo, “CW HI Laser Based on a Stationary Inverted Lyman Population Formed from Incandescently Heated Hydrogen Gas with Certain Group I Catalysts,” IEEE Transactions on Plasma Science, Vol. 31, No. 2, (2003), pp. 236-247.
34. R. L. Mills, P. Ray, “Stationary Inverted Lyman Population Formed from Incandescently Heated Hydrogen Gas with Certain Catalysts,” J. Phys. D, Applied Physics, Vol. 36, (2003), pp. 1504-1509.
35. R. L. Mills, P. Ray, “Extreme Ultraviolet Spectroscopy of Helium-Hydrogen Plasma,” J. Phys. D, Applied Physics, Vol. 36, (2003), pp. 1535-1542.
36. R. L. Mills, P. Ray, B. Dhandapani, M. Nansteel, X. Chen, J. He, “New Power Source from Fractional Quantum Energy Levels of Atomic Hydrogen that Surpasses Internal Combustion,” J Mol. Struct., Vol. 643, No. 1-3, (2002), pp. 43-54.
37. R. Mills, P. Ray, “Spectral Emission of Fractional Quantum Energy Levels of Atomic Hydrogen from a Helium-Hydrogen Plasma and the Implications for Dark Matter,” Int. J. Hydrogen Energy, Vol. 27, No. 3, (2002), pp. 301-322.
38. R. Mills, P. Ray, R. M. Mayo, “The Potential for a Hydrogen Water-Plasma Laser,” Applied Physics Letters, Vol. 82, No. 11, (2003), pp. 1679-1681.
39. J. Phillips, R. L. Mills, X. Chen, “Water Bath Calorimetric Study of Excess Heat in ‘Resonance Transfer’ Plasmas,” Journal of Applied Physics, Vol. 96, No. 6, pp. 3095-3102.
40. R. L. Mills, X. Chen, P. Ray, J. He, B. Dhandapani, “Plasma Power Source Based on a Catalytic Reaction of Atomic Hydrogen Measured by Water Bath Calorimetry,”

Thermochimica Acta, Vol. 406/1-2, (2003), pp. 35-53.

41. R. Mills, B. Dhandapani, M. Nansteel, J. He, T. Shannon, A. Echezuria, "Synthesis and Characterization of Novel Hydride Compounds," Int. J. of Hydrogen Energy, Vol. 26, No. 4, (2001), pp. 339-367.
42. R. Mills, B. Dhandapani, N. Greenig, J. He, "Synthesis and Characterization of Potassium Iodo Hydride," Int. J. of Hydrogen Energy, Vol. 25, Issue 12, December, (2000), pp. 1185-1203.
43. R. Mills, B. Dhandapani, M. Nansteel, J. He, A. Voigt, "Identification of Compounds Containing Novel Hydride Ions by Nuclear Magnetic Resonance Spectroscopy," Int. J. Hydrogen Energy, Vol. 26, No. 9, (2001), pp. 965-979.
44. R. L. Mills, P. Ray, B. Dhandapani, R. M. Mayo, J. He, "Comparison of Excessive Balmer α Line Broadening of Glow Discharge and Microwave Hydrogen Plasmas with Certain Catalysts," J. of Applied Physics, Vol. 92, No. 12, (2002), pp. 7008-7022.
45. R. L. Mills, P. Ray, "Substantial Changes in the Characteristics of a Microwave Plasma Due to Combining Argon and Hydrogen," New Journal of Physics, www.njp.org, Vol. 4, (2002), pp. 22.1-22.17.
46. R. L. Mills, P. C. Ray, R. M. Mayo, M. Nansteel, B. Dhandapani, J. Phillips, "Spectroscopic Study of Unique Line Broadening and Inversion in Low Pressure Microwave Generated Water Plasmas," J. Plasma Physics, Vol. 71, Part 6, (2005), pp. 877-888.
47. C. Barbeau, J. Jolly, "Spectroscopic investigation of energetic atoms in a DC hydrogen glow discharge," Journal of Physics, D, Applied Physics, Vol. 23, (1990), pp. 1168-1174.
48. S. A. Bzenic, S. B. Radovanov, S. B. Vrhovac, Z. B. Velikic, and B. M. Jelenkovic, Chem. Phys. Lett., Vol. 184, (1991), pp. 108-112.
49. E. L. Ayers, W. Benesch, "Shapes of atomic-hydrogen lines produced at a cathode surface," Physical Review A, Vol. 37, No. 1, (1988), pp. 194-199.
50. W. Benesch, E. Li, "Line shapes of atomic hydrogen in hollow-cathode discharges," Optic Letters, Vol. 9, No. 8, (1984), pp. 338-340.
51. C. Chen, T. Wei, L. R. Collins, and J. Phillips, "Modeling the discharge region of a microwave generated hydrogen plasma," J. Phys. D: Appl. Phys., Vol. 32, (1999), pp. 688-698.
52. A. Bogaerts, R. Gijbels, "Effects of adding hydrogen to an argon glow discharge: overview of some relevant processes and some quantitative explanations," Journal of Analytical Atomic Spectroscopy, Vol. 15, (2000), pp. 441-449.
53. W. L. Wiese, *Plasma Diagnostics Technique*, Ed. R. H. Huddelstone and S. L. Leonard, Academic Press, New York, (1965), p. 265.

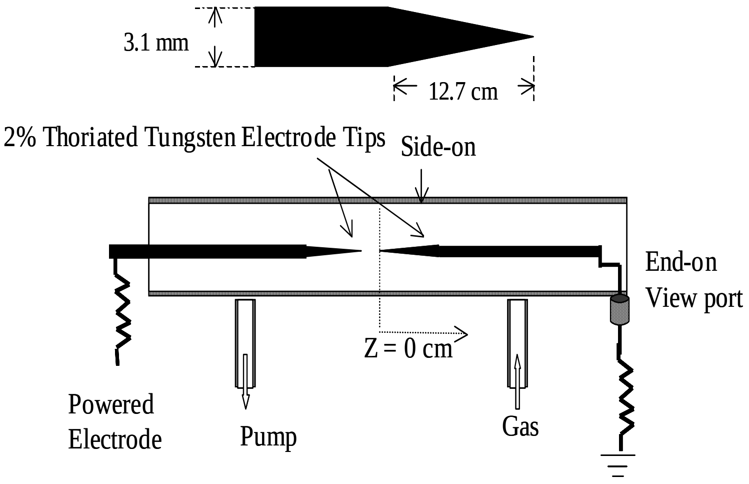


Figure 1. Schematic of the DC discharge created between the fine tips of 2% thoriated tungsten electrodes with the direction of axial scans defined. The cathode tip is taken as z=0 cm for side-on observations measured along the axis of the cathode from its tip to its electrical connection.

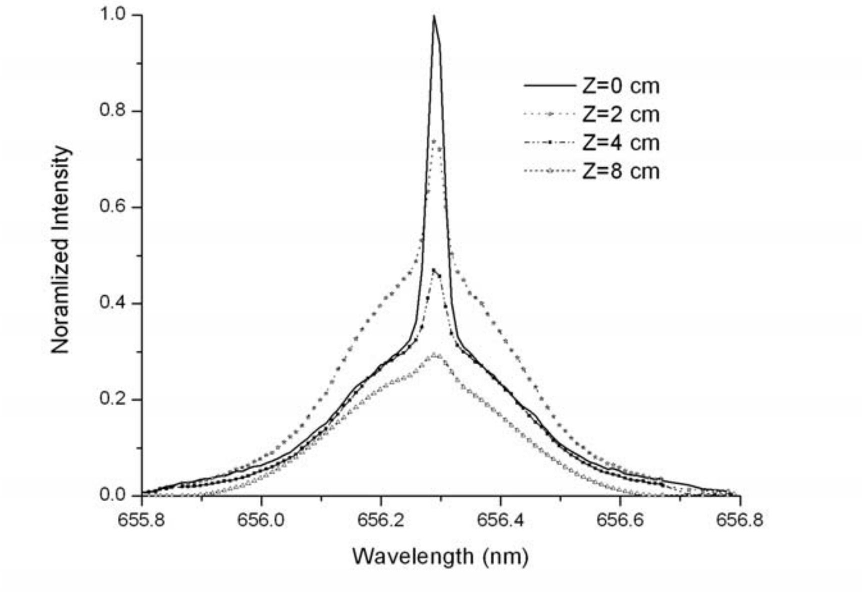


Figure 2. Axial scan of the 656.3 nm Balmer α line width recorded on a 1 Torr Ar/H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA showing 75% of the excited hydrogen atom (n=3 state) population was "hot" with an average hydrogen atom energy of 40 eV, compared to <1 eV for the slow population. The intensity, but not the broadening, changed with position in the cell indicating that the broadening was not dependent on the electric field.

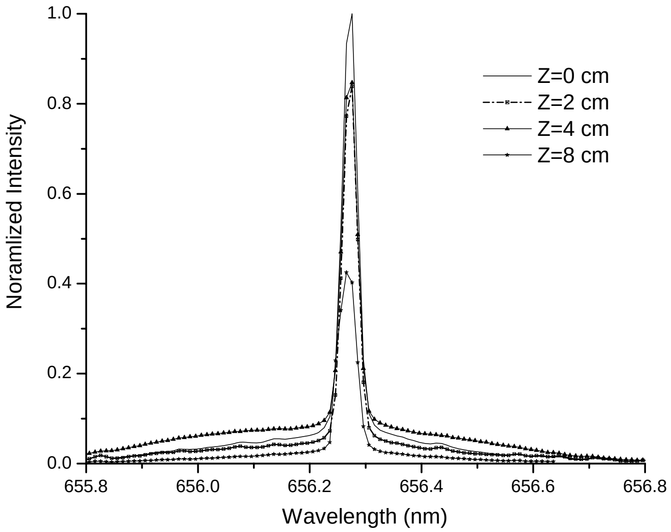


Figure 3. Axial scan of the 656.3 nm Balmer α line width recorded on a 1 Torr He/H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA showing 50% of the excited hydrogen atom (n=3 state) population was "hot" with an average hydrogen atom energy of 45 eV, compared to <1 eV for the slow population. The intensity, but not the broadening, changed with position in the cell indicating that the broadening was not dependent on the electric field.

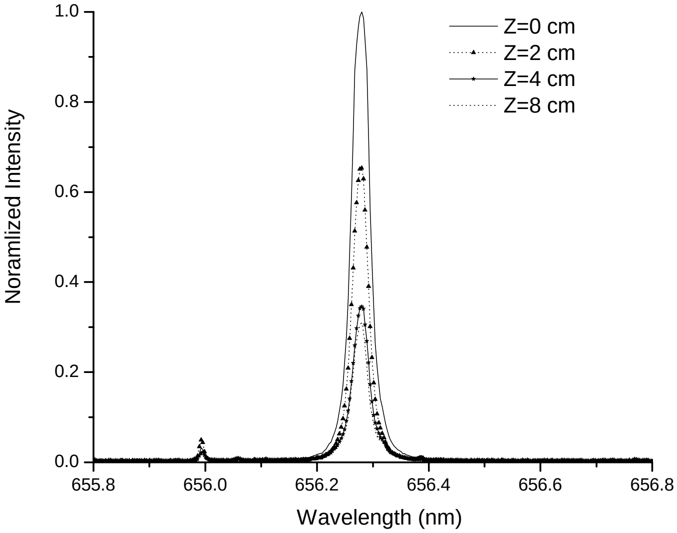
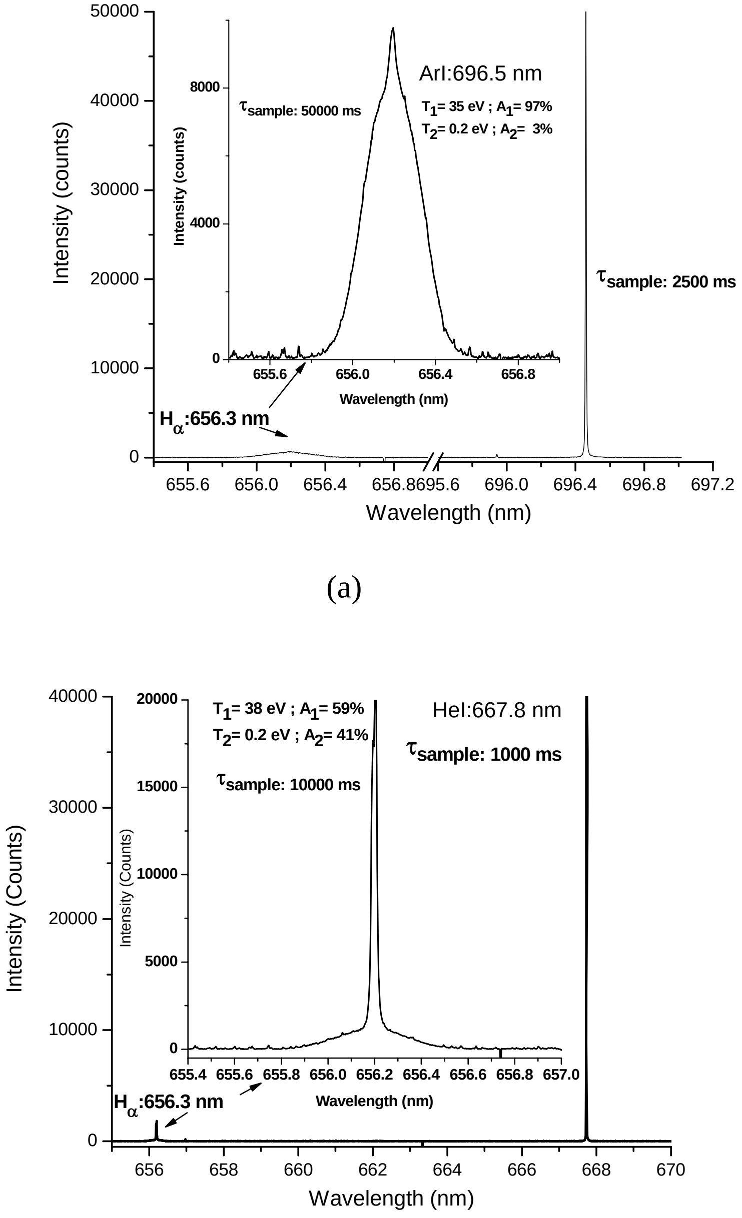


Figure 4. Axial scan of the 656.3 nm Balmer α line width recorded on a 1 Torr Xe/H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA showing only a cold population of <1 eV with a decrease in intensity along the cathode.



(a)

(b)

Figure 5. (a) The 696.54 *nm* *Ar* I line width for a 1 Torr Ar plasma with trace hydrogen at 400 V and 20 mA. (b) The 667.816 *nm* *He* I line width for a 1 Torr He plasma with trace hydrogen at 400 V and 20 mA. No broadening was observed in either case for Ar and He atoms; whereas, the hydrogen atoms have energies of about 35-40 eV.

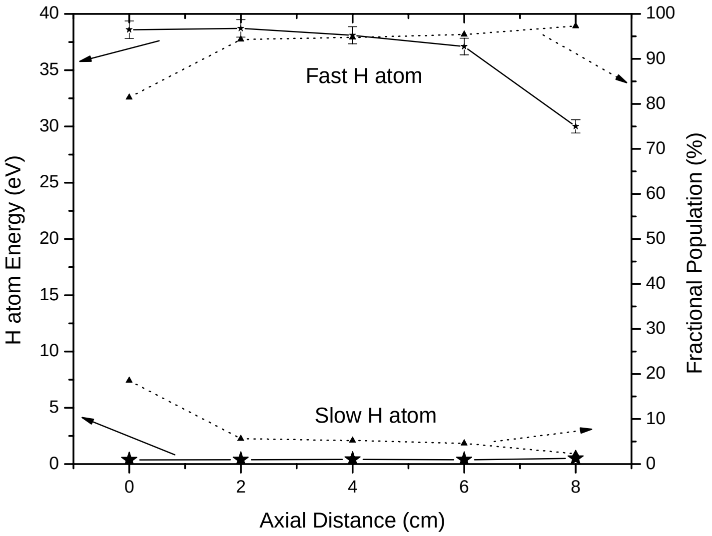


Figure 6. Axial plots of atom temperature and fractional population (given by the relative area under the curve) of excited (n=3) fast hydrogen atoms corresponding to the spectrum in Figure 2. Very energetic hydrogen population is present even at a distance of 8 cm away from the cathode tip, where most of the potential falls.

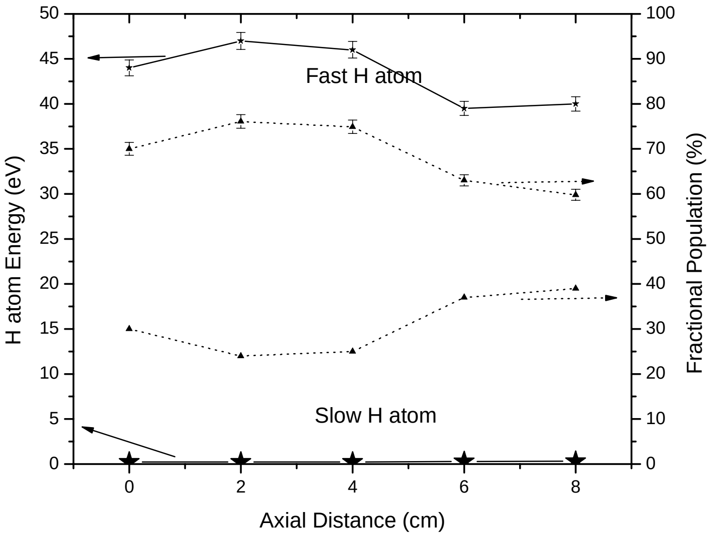


Figure 7. Axial plots of temperature and population (given by the relative area under the curve) of excited (n=3 state) hydrogen atoms corresponding to the spectrum in Figure 3. Here, also a very energetic hydrogen population was present even at a distance of 8 cm away from the cathode tip, where most of the potential falls.

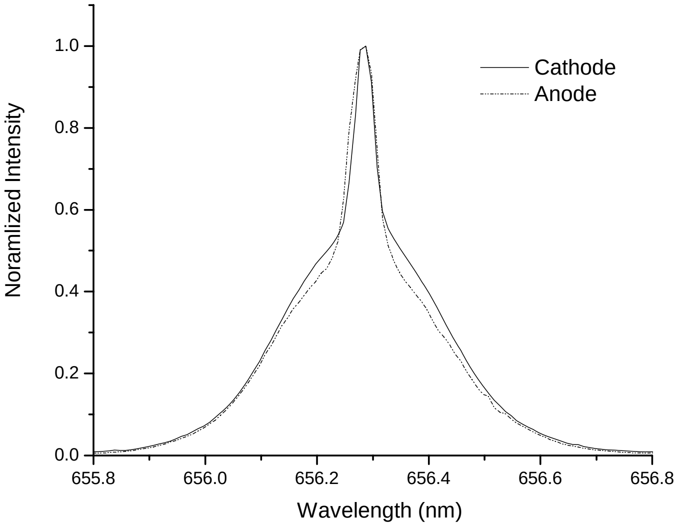


Figure 8. The 656.3 nm Balmer α line width recorded end-on (parallel to the electric field) on a 1 Torr Ar/H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA. Both views looking towards the cathode as well as the anode show a symmetrical emission profile. The temperature of hot hydrogen atoms was in the range of 38-40 eV.

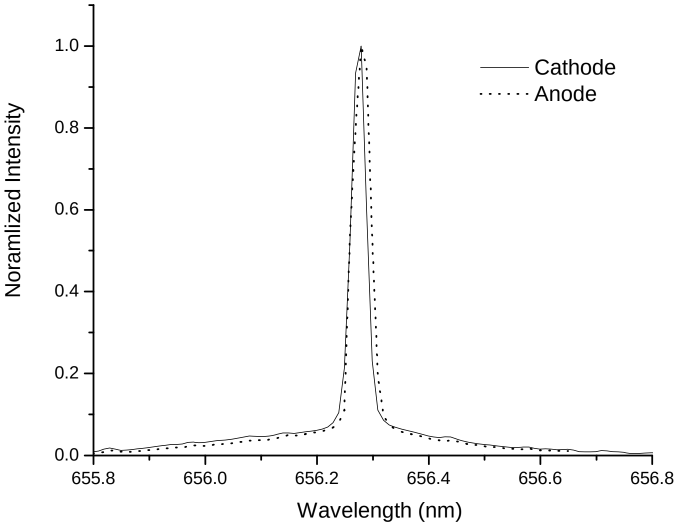


Figure 9. The 656.3 nm Balmer α line width recorded end-on (parallel to the electric field) on a 1 Torr He/H_2 (95/5%) DC plasma discharge with needle-like electrodes at 400 V and 20 mA. Both views looking towards the cathode as well as the anode showed a symmetrical emission profile. The temperature of hot hydrogen atoms was in the range of 40-43 eV.

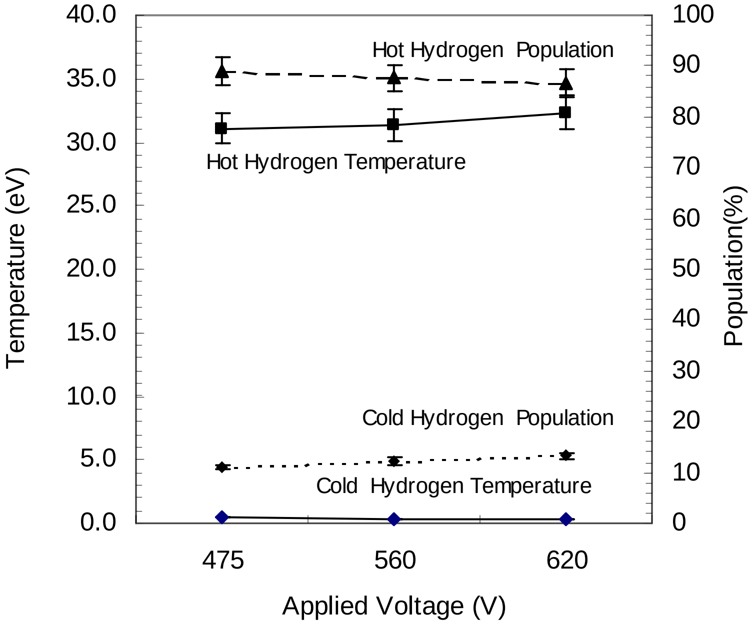


Figure 10. The energies and populations determined on the two-component profile of the 656.3 nm Balmer α line width of 1 Torr Ar/H_2 (95/5%) DC plasma discharges with needle-like electrodes recorded side-on at z=4 cm for 4.75 W (475 V; 10 mA), 16.8 W (560 V; 30 mA), and 24.8 W (620 V; 40 mA). The average fast-hydrogen atom energy of 31-32 eV did not change with applied voltage over the range 475 V to 620 V indicating that the broadening was not dependent on the electric field.

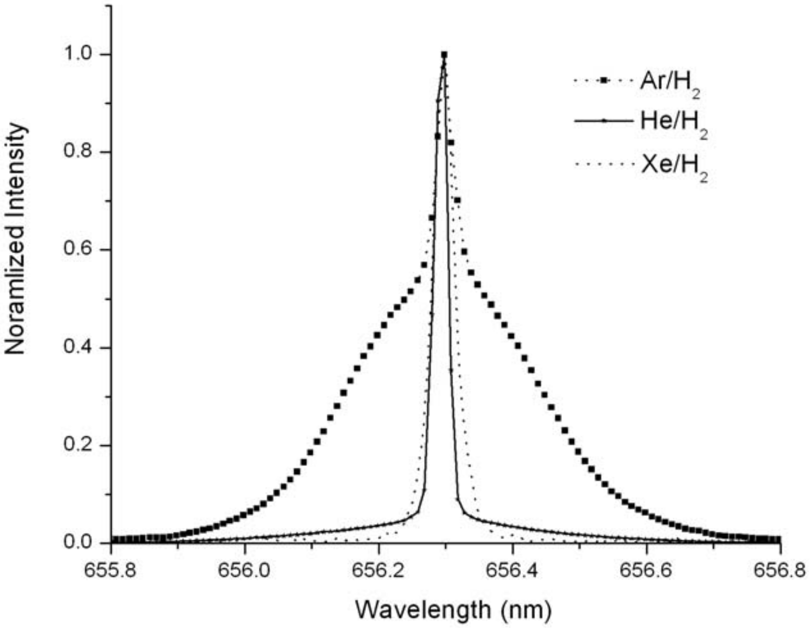


Figure 11. Normalized end-on emission spectra of 1 Torr Ar/H_2 (95/5%), 1 Torr He/H_2 (95/5%), and 1 Torr Xe/H_2 (95/5%) plasmas looking towards the cathode that show a symmetrical emission profile.

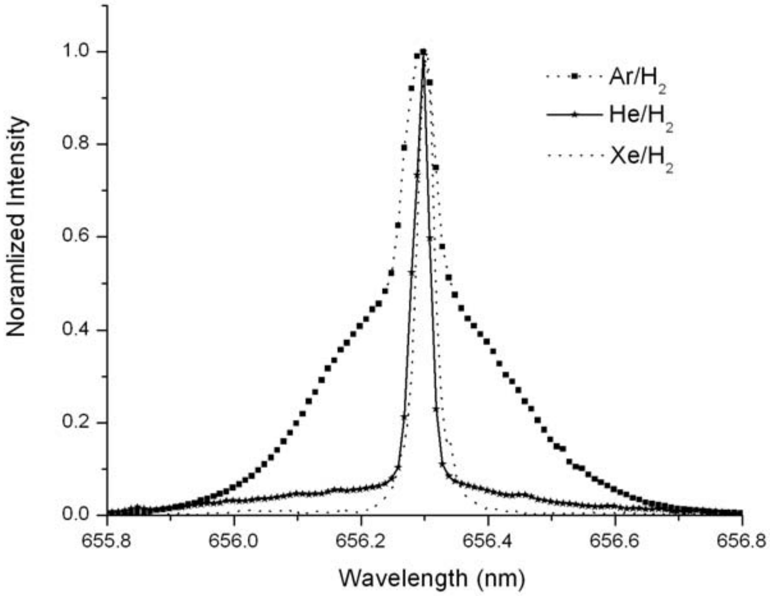


Figure 12. Normalized end-on emission spectra of 1 Torr Ar/H_2 (95/5%), 1 Torr He/H_2 (95/5%), and 1 Torr Xe/H_2 (95/5%) plasmas looking towards the anode that show the symmetrical emission profile.

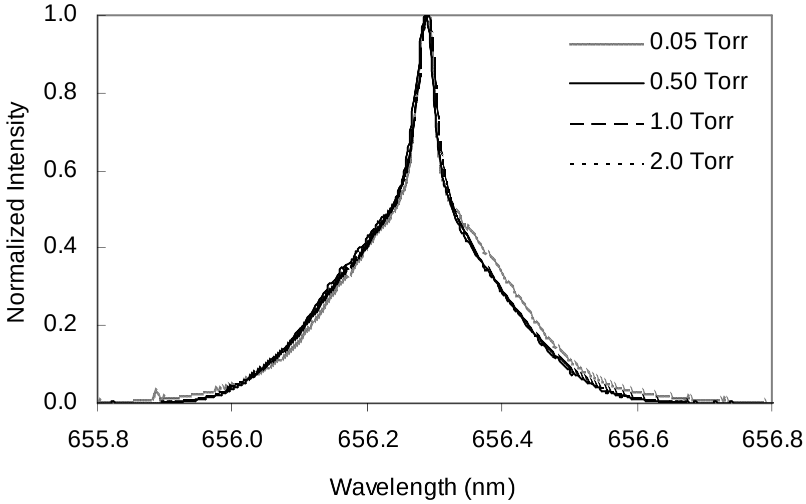


Figure 13. Normalized 656.3 nm Balmer α line width on Ar/H_2 (95/5%) DC plasma discharges with needle-like electrodes recorded side-on at z=4 cm at 400 V and 20 mA as the pressure was varied from 0.05 Torr to 2 Torr. The symmetrical peak shape of the fast population was not dependent on the gas pressure.

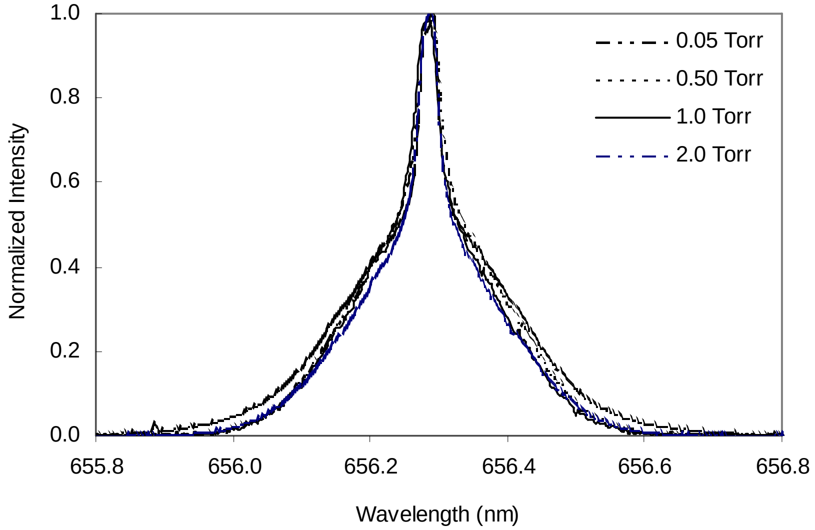


Figure 14. Normalized 656.3 nm Balmer α line widths on Ar/H_2 (95/5%) DC plasma discharges with needle-like electrodes recorded end-on looking at the cathode at 400 V and 20 mA as the pressure was varied from 0.05 Torr to 2 Torr. The symmetrical peak shape of the fast population was not dependent on the gas pressure.