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Fast H in Hydrogen Mixed Gas Microwave Plasmas When an Atomic Hydrogen Supporting Surface was Present

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ABSTRACT

Atomic hydrogen is heated to temperatures of up to two orders of magnitude greater than the electron temperature or the temperature of any other species in certain hydrogen mixed gas RF or glow discharge plasmas. A crucial test of energetic hydrogen chemistry regarding a resonant energy transfer or rt-mechanism (RTM) versus field acceleration models (FAM) as the basis of this selective isotropic heating of a population of extraordinarily high-kinetic-energy hydrogen atoms is the observation of fast H in microwave cells proven to lack a high field as shown by the complete absence of fast H (~0.08 eV) by Jovicevic et al. [S. Jovicevic, N. Sakan, M. Ivkovic, N. Konjevic, J. Appl. Phys. 105, 013306-1 (2009)]. The RTM predicts an enhancement in the production of fast H with the presence of a surface to support a high concentration of hydrogen atoms in order to initiate the energetic hot-H source reaction that then propagates isotropically throughout the plasma. In contrast to the prior results, extraordinarily fast H of greater than 4 eV (50 times that observed and deemed possible in the Evenson microwave cell by FAM advocate Jovicevic et al.) and 50% fractional population was observed as predicted for RTM using the catalytic reaction systems of He/H₂, Ar/H₂, pure H₂, and water vapor microwave plasmas when an electrically insulating, but atomic-hydrogen supporting material was placed in the plasma region. Increasing concentrations of Xe in the non-catalytic Xe/H₂ system results in a significant decrease in the energy and population of fast excited-state H atoms.

Key Words: hydrogen mixed gas microwave plasmas, catalysis, fast hydrogen, Balmer line broadening, hydrogen dissociator

I. Introduction

Classical physics (CP) gives closed-form solutions of the hydrogen atom, the hydride ion, the hydrogen molecular ion, and the hydrogen molecule and predicts corresponding species having fractional principal quantum numbers [2–14]. The nonradiative state of atomic hydrogen, which is historically called the “ground state” forms the basis of the boundary condition of CP to solve the bound electron. CP predicts a reaction involving a resonant, nonradiative energy transfer from otherwise stable atomic hydrogen to a catalyst capable of accepting the energy to form hydrogen in lower-energy states than previously thought possible. Specifically, CP predicts that atomic hydrogen may undergo a catalytic reaction with certain atoms, excimers, ions, and diatomic hydrides which provide a reaction with a net enthalpy of an integer multiple of the potential energy of atomic hydrogen, $E_n = 27.2 \text{ eV}$ where E_h is one Hartree. Specific species (e.g. He^+ , $2H$, Ar^+ , Sr^+ , K , Li , HCl , and NaH) identifiable on the basis of their known electron energy levels are required to be present with atomic hydrogen to catalyze the process. The reaction involves a nonradiative energy transfer of an integer multiple of 27.2 eV from atomic hydrogen to the catalyst followed by $q \cdot 13.6 \text{ eV}$ continuum emission or $q \cdot 13.6 \text{ eV}$ transfer to another H to form extraordinarily hot, excited-state H and a hydrogen atom that is lower in energy than unreacted atomic hydrogen that corresponds to a fractional principal quantum number. That is, in the formula for the principal energy levels of the hydrogen atom:

$$E_n = -\frac{e^2}{n^2 8\pi\epsilon_0 a_H} = -\frac{13.598 \text{ eV}}{n^2} \quad (1)$$

$$n = 1, 2, 3, \dots \quad (2)$$

where a_H is the Bohr radius for the hydrogen atom (52.947 pm), e is the magnitude of the charge of the electron, and ϵ_0 is the vacuum permittivity, fractional quantum numbers:

$$n = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots, \frac{1}{p}; \quad p \leq 137 \text{ is an integer} \quad (3)$$

replace the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states. The $n = 1$ state of hydrogen and the $n = \frac{1}{\text{integer}}$ states of hydrogen are nonradiative, but

a transition between two nonradiative states, say $n = 1$ to $n = 1/2$, is possible via a nonradiative energy transfer. Hydrogen is a special case of the stable states given by Eqs. (1) and (3) wherein the corresponding radius of the hydrogen or hydrino atom is given by

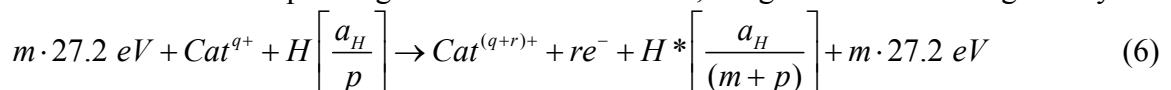
$$r = \frac{a_H}{p}, \quad (4)$$

where $p = 1, 2, 3, \dots$. In order to conserve energy, energy must be transferred from the hydrogen atom to the catalyst in units of

$$m \cdot 27.2 \text{ eV}, \quad m = 1, 2, 3, 4, \dots \quad (5)$$

and the radius transitions to $\frac{a_H}{m+p}$. The catalyst reactions involve two steps of energy release

[2, 15]: a nonradiative energy transfer to the catalyst followed by additional energy release as the radius decreases to the corresponding stable final state. Thus, the general reaction is given by



$$H^* \left[\frac{a_H}{(m+p)} \right] \rightarrow H \left[\frac{a_H}{(m+p)} \right] + [(m+p)^2 - p^2] \cdot 13.6 \text{ eV} - m \cdot 27.2 \text{ eV} \quad (7)$$

$$Cat^{(q+r)+} + re^- \rightarrow Cat^{q+} + m \cdot 27.2 \text{ eV} \quad (8)$$

And, the overall reaction is

$$H \left[\frac{a_H}{p} \right] \rightarrow H \left[\frac{a_H}{(m+p)} \right] + [(m+p)^2 - p^2] \cdot 13.6 \text{ eV} \quad (9)$$

q , r , m , and p are integers. $H^* \left[\frac{a_H}{(m+p)} \right]$ has the radius of the hydrogen atom (corresponding to the 1 in the denominator) and a central field equivalent to $(m+p)$ times that of a proton, and $H \left[\frac{a_H}{(m+p)} \right]$ is the corresponding stable state with the radius of $\frac{1}{(m+p)}$ that of H . As the electron undergoes radial acceleration from the radius of the hydrogen atom to a radius of $\frac{1}{(m+p)}$ this distance, energy is released as characteristic light emission or as third-body kinetic energy. The emission may be in the form of an extreme-ultraviolet continuum radiation having an edge at $[(m+p)^2 - p^2 - 2m] \cdot 13.6 \text{ eV}$ ($\frac{912}{[(m+p)^2 - p^2 - 2m]} \text{ \AA}$) and extending to longer wavelengths. In addition to radiation, a resonant kinetic energy transfer to form fast H may occur. Subsequent excitation of these fast $H(n=1)$ atoms by collisions with the background H_2 followed by emission of the corresponding $H(n=3)$ fast atoms gives rise to broadened Balmer α emission.

Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2 \text{ eV}$ (i.e. it resonantly accepts the nonradiative energy transfer from hydrogen atoms and releases the energy to the surroundings to affect electronic transitions to fractional quantum energy levels). As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (1) and (3). Thus, the catalysis releases energy from the hydrogen atom with a commensurate decrease in size of the hydrogen atom, $r_n = na_H$ where n is given by Eq. (3). For example, the catalysis of $H(n=1)$ to $H(n=1/4)$ releases 204 eV , and the hydrogen radius decreases from a_H to $\frac{1}{4}a_H$. The catalyst product, $H(1/p)$, may also react with an electron to form a hydrino hydride ion $H^-(1/p)$, or two $H(1/p)$ may react to form the corresponding molecular hydrino $H_2(1/p)$.

The second ionization energy of helium is 54.4 eV ; thus, the ionization reaction of He^+ to He^{2+} has a net enthalpy of reaction of 54.4 eV which is equivalent to $2 \cdot 27.2 \text{ eV}$. Furthermore, 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 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 228 Å 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 (1) helium with hydrogen and (2) 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 predicted EUV continuum, the product gas $H_2(1/4)$, power [16], and extraordinary (>50 eV) Balmer α line broadening were observed [15].

Similarly, Ar^+ may serve as a catalyst since its ionization energy is about 27.2 eV. The catalyst reaction of Ar^+ to Ar^{2+} forms $H(1/2)$ which may further react to form $H(1/4)$ and $H_2(1/4)$ [2]. Since the ionization energy of Sr^+ to Sr^{3+} has a net enthalpy of reaction of 2·27.2 eV, Sr^+ may also serve as catalyst alone or with Ar^+ catalyst to form $H_2(1/4)$. A further signature of the energetic H chemistry was the observation of the formation of a plasma called a resonant transfer- or rt-plasma at low temperatures (e.g. $\approx 10^3$ K) and very low field strengths of about 1-2 V/cm when a hydrino catalyst was present with atomic hydrogen [15, 17–27]. It was reported previously that an rt-plasma formed with a low field (1V/cm), at low temperatures (e.g. $\approx 10^3$ K), from atomic hydrogen generated at a tungsten filament and strontium which was vaporized by heating the metal [19–24]. Strong EUV emission was observed that increased with the addition of argon, but not when sodium, magnesium, or barium replaced strontium or with hydrogen, argon, or strontium alone. Time-dependent line broadening of the H Balmer α line was observed corresponding to extraordinarily fast H (25 eV) [23]. Thus, line broadening is just one aspect of a prior undiscovered energetic reaction to form a new state of hydrogen.

Independently, a controversy has emerged regarding the origin of a population of extraordinarily high-energy hydrogen in certain hydrogen mixed gas plasmas. The opposing theories are various field acceleration models/Collisional Model (FAM/CM) [28–47] wherein the energy source is the applied electric field and the resonance transfer reaction or mechanism (RTM) wherein the energy source is energetic hydrogen chemistry that occurs isotropically and selectively heats H (Eqs. (6-9)) [15, 17, 18, 23, 27, 48–56]. A common feature of the former is that positive ions are accelerated in the electric field of the negatively biased electrode, and the energy is ultimately deposited selectively and exclusively with excited-state H atoms by several postulated energy or electron transfer reactions [28–47]. The selectivity for H is a critical and unusual feature of this phenomenon since counter to expectations, no other ions, atoms, or molecules are hot; nor, are the electrons hot. It is for certain that the energy must have a source, and it is trivial to propose that the source is the applied electric field. However, the high energy H is observed in regions of the cell where there is no high field, and based on collisional cross

sections, it is impossible for high energy H to be created in the high field region and traverse the plasma gas matrix to regions where it is observed at the same energy as at the cathode. Thus, it is difficult to explain why the energetic H is produced at the same energy in regions where there is no field as it is in the highest-field regions [15, 34, 45, 48–56] or why time-dependent hot H is observed in rt-plasmas having a very low field [17, 18, 23, 27]. Electron heating of H is not possible especially given that the H energy and populations are up to 100 times the electron energy and density [15, 48–56]. Another challenge is the observation that the hot H population is nondirectional even though the acceleration is only in the direction of the field. Here, hydrogen atoms are postulated to be perfectly reflected from the cathode and diverted in all directions by collisions with background gasses [34, 45, 48, 49]. The experimental evidence does not support this aspect in that there is no FAM predicted dependence on the gas pressure, accelerating voltage, or physical cross section or the nature of the cathode [48, 49]. Additional aspects are that the energy is dependent on the presence of certain species such as Ar^+ as opposed to Xe^+ , identified in the RTM and not the FAM as reactants. The energetic H production has further features of a chemical reaction such as its dependencies on the time of reaction and the build up of intermediates by restricting flow [15, 48, 49, 53].

Recently, advocates of FAMs have shown conclusively that the electric field is effectively zero in an Evenson microwave plasma as evidenced by the complete absence of fast H to about the limit of measurement imposed by the instrument width (~ 0.08 eV compared to the electron excitation temperature of 0.13 eV) [1]. Thus, the converse is true—if fast H is found in microwave plasmas of the same gasses that show fast H in other systems, the field acceleration model is disproved [47]. Mills et al. working in another area, energetic H chemistry [2, 15, 17, 18, 23, 27, 48–56] predicted that such high energy H would be produced in certain plasmas particularly He/ H_2 , Ar/ H_2 , water vapor (reported for the first time [53] with an energy >150 eV, higher than any FAM can explain [29]), and pure H_2 glow discharge and RF plasmas, and that the presence of a metal surface should enhance the production of fast H by supporting a high concentration of H atoms to initiate the high energy H chemistry that subsequently propagates throughout the H containing plasma. In this case, isotropic high energy H is anticipated consistent with all aspects of the data recorded on plasma cells [15, 17, 18, 23, 27–56]. In principle, it should be possible to achieve sufficient kinetics to see substantial fast H in the microwave plasmas as well. One aspect of the microwave plasma is that it is weakly ionized and lacks a high-energy electron component to excite fast H to emit Balmer emission before it cools, making it more difficult to observe even if fast H is present. Another aspect is that it lacks a metal surface to support atomic H in contrast to other plasma sources that possess metal electrodes. It was reported previously that a high concentration of atomic H is formed in a water vapor RF cell [53] wherein several monolayers of atomic H can initially form on the cathode surface to initiate the energetic H reaction [57–60]. On the contrary, the prevention of the formation of surface atomic hydrogen prevents the reaction [36]. If the same processes were occurring in microwave plasmas that produce greater than 50 eV hot H and populations over about 50% in glow discharge and RF cells, then it should be possible to achieve sufficient kinetics to overcome the plasma characteristic limitation of the slow rate of excitation versus hot H cooling.

In this paper, we report that fast H was not detectable in hydrogen mixed gas microwave plasmas until a material having a surface to support layers of atomic hydrogen was placed in the plasma region. Electrically insulating commercial hydrogen supporting surfaces such as alumina powder as well as 1%Pd on alumina powder were placed inside an alumina boat that extended

past the length of plasma region. Thus, the spectroscopic observation of broadened Balmer line widths as a measure of fast H as the chemical conditions favorable to RTM and irrelevant to FAM were applied, served as a definitive test of RTM over FAM. As a further refutation of the basic physics of FAM regarding any potential field that may exist at the beads due to any mechanism, a high-bias voltage was applied to the 1%Pd/Al₂O₃ powder placed on a metal foil with no change in the broadening. Specifically, FAM predicts a significant variation in the H_α field emission profile and consequently the energy and fractional population of H atoms as the biasing potential is varied from -250V to +250V, but none was observed.

II. Experimental

The schematic of the microwave plasma system is shown in Figure 1. The experimental set up comprised a microwave discharge gas cell light source and a high-resolution visible spectrometer described previously [15]. Emission spectra were obtained on microwave plasmas of pure H₂, water vapor, and gas mixtures of 50%He/50%H₂ and 50%Xe/ 50% H₂. The microwave generator was a Sairem (GMP03KS, 2.45 GHz, 300W), and the plasma was produced inside a (1/2"x10") quartz tube using a Sairem coaxial microwave cavity (Evenson cavity). The net microwave power delivered to the plasma was set at 20 watts. In a “flow” mode, the gas pressure inside the cell was maintained by flowing the gas while monitoring the pressure with a 10 Torr MKS Baratron absolute pressure gauge. Additionally, the plasmas were maintained at a constant pressure in a “batch” mode with the pump closed. High-resolution visible spectra were recorded on plasmas without the hydrogen supporting surface as well as in the presence of electrically insulating commercial hydrogen supporting surfaces such as alumina powder as well as 1%Pd on alumina powder placed inside an alumina boat that extended past the length of plasma region. In this paper we present our results for commercial hydrogenation catalyst 1% Pd/Al₂O₃ (Alfa-Aesar: catalog number: 11711, 400 mesh powder, 99.9%) loaded inside an alumina boat (Al-23; Alfa-Aesar: catalog number: 33174; 69 mm x 9 mm x 6 mm).

The Balmer line widths were measured using a high-resolution visible spectrometer. The plasma emission was fiber-optically coupled to a Jobin Yvon Horiba 1250 M spectrometer described previously [15, 48, 49] through a high-quality UV (2000-8000 Å) fiber-optic bundle and a 220F matching fiber adapter with an aperture of 0.12 and a corresponding acceptance angle of 12°. The spectrometer had a 1250 mm focal length with a 2400 g/mm grating and a detector comprising a photomultiplier tube (PMT) with a stand-alone power supply of 995 volts or a Symphony model, liquid-nitrogen cooled, back illuminated 2048×512 CCD array with an element size of 13.5 μm × 13.5 μm, 16 bit ADC, and 20 kHz and 1 MHz read outs. Using the 5460 Å Hg I line from a NIST calibrated mercury lamp with the entrance and exit slits set to 40 μm, the measured CCD resolution due to the finite-pixel-spectral width was very high, ±0.06 Å. The spectrometer accuracy was ±0.5 Å, and its repeatability was ±0.05 Å. The spectrometer was scanned through the emission profiles of helium and the Balmer lines with a step size of 0.1 Å at entrance and exit slit-widths of 20 μm.

The hydrogen atom Doppler energies were calculated from the width of the 6563 Å Balmer α line emitted from the microwave plasmas [61]. Each Balmer α spectral line was fit using one or two Gaussian curves: one for the “slow” (<1 eV) hydrogen and the second for “fast” (>4 eV) hydrogen. The full half-width Δλ_G of each Gaussian results from the Doppler (Δλ_D) and instrumental (Δλ_I) half-widths:

$$\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2} \quad (10)$$

The measured half-width $\Delta\lambda_l$ of $\pm 0.06 \text{ \AA}$ was negligible. Thus, the temperature was calculated from the Doppler half-width using the formula:

$$\Delta\lambda_D = 7.16 \times 10^{-7} \lambda_0 \left(\frac{T}{\mu} \right)^{1/2} \quad (11)$$

where λ_0 is the line wavelength, T is the temperature in K ($1 \text{ eV} = 11,605 \text{ K}$), and μ is the molecular weight (=1 for atomic hydrogen). In each case, the error in the average Doppler half-width over 5 scans was about $\pm 5\%$ that was attributed predominately to fluctuations in the plasma.

In addition, $T_{excitation}$ was measured on microwave discharge plasmas of hydrogen from the ratio of the intensity of the Balmer lines, and $T_{excitation}$ was measured on He/H₂ (5%) plasmas from the ratio of the intensity of the *He* atomic lines as described previously [50, 51]. The electron density n_e and temperature T_e were determined using a Langmuir probe according to the method given previously [51, 53].

In order to test the effect of field potential variation on the H atom energy, the 1%Pd/Al₂O₃ powder was placed on a metal foil inside the quartz tube. The metal foil was attached to a bipolar DC power supply wherein the metal foil acted as a biased substrate as the biasing potential was varied from -250V to +250V. The Balmer line widths were recorded as a function of the bias voltage.

III. Results and Discussion

Emission spectra were obtained on microwave plasmas of pure H₂, water vapor, and gas mixes of 50%He/50%H₂ and 50%Xe/ 50% H₂ at 30 mTorr with a net coupled microwave power of $\sim 20 \text{ W}$. In the absence of a hydrogen-support material, the Balmer α line profiles of the pure H₂, He/H₂, and water vapor microwave plasma emission each comprised only one narrow Gaussian corresponding to an H temperature of less than 0.1-0.2 eV consistent with the observation of Jovicevic et al [1]. A representative emission profile for 30 mTorr He/H₂ plasma in the absence of a hydrogen-support material is shown in Figure 2. In contrast, when the alumina boat filled with 1%Pd/Al₂O₃ powder was placed under the Evenson microwave applicator, the Balmer α line profiles of the plasma emission (Figure 3(a)) each comprised two distinct Gaussian peaks, an inner, narrower peak corresponding to a slow component with an average hydrogen energy of $\sim 0.3 \text{ eV}$ and an outer, broader peak corresponding to a fast component with an energy of $\sim 4.8 \text{ eV}$ and a fractional population of fast H atoms in the excited ($n=3$) state of $\sim 22\%$ (Figure 3(b)). The slow population is assigned to thermal excitation in the plasma and matches those reported previously [15, 17, 18, 23, 27–56].

Figure 4 shows the Balmer α and HeI emission profile for a 30 mTorr He/H₂ discharge in the flow mode with net microwave power of 20W. No broadening was observed for the 6678 \AA HeI line; whereas, the Balmer α emission profile shows the presence of fast H atoms with an energy $\sim 4.8 \text{ eV}$ and a fractional population of fast H atom in the excited ($n=3$) state of 22%. In the batch mode, premixed gas was introduced into the plasma tube using a needle valve with the vacuum pump closed. As shown in Figure 5, there was a significant increase in the fractional population of fast H atoms in the excited ($n=3$) state that demonstrates an extraordinary heating process wherein the majority of H atoms (63%) in the excited ($n=3$) state are fast with an energy $\sim 2.8 \text{ eV}$. Similar results were obtained with Ar/H₂ plasmas.

Extraordinary fast H results were further obtained for pure hydrogen plasmas as well as

water vapor plasmas as predicted in both the flow mode as well as the batch mode. Figures 6 and 7 show the emission profiles of 30 mTorr pure H₂ plasmas in the flow and batch modes, respectively. The energy and fractional population of fast H atoms in the excited (n=3) state are 4.2 eV; 25% and 2.7 eV; 52%, respectively. Similarly, Figure 8 shows the emission profile of a 30 mTorr water vapor plasma in the batch mode corresponding to fast atoms with an energy of ~2.7 eV and a fractional H atoms population in the excited (n=3) state of ~62%. In contrast, the Doppler width and corresponding energy and fractional population of fast excited-state (n=3) H atoms decreased when Xe was added to the hydrogen plasma as shown in Figure 9. The normalized emission profiles clearly indicate that there is a decrease in energy as well as the fractional population of fast H atoms in the excited (n=3) state from 2.83 eV and 63% for the He/H₂ discharge to 1.4 eV and 8% for the Xe/H₂ discharge.

The Langmuir-probe determined electron density n_e was $10^9 - 10^{10} \text{ cm}^{-3}$ and the electron temperature T_e was less than 1 eV. These numbers are consistent with reported Langmuir probe measurements for the electron density n_e for capacitively coupled RF, glow discharge, inductively coupled RF, and microwave plasma cells that showed selective, excessive fast H wherein the respective electron densities were $10^{10} - 10^{11} \text{ cm}^{-3}$ [41, 43], $10^9 - 10^{11} \text{ cm}^{-3}$ [32], 10^9 cm^{-3} [62], and $< 10^9 \text{ cm}^{-3}$ [51]. Given that the low electron density and temperature eliminate all other mechanisms [15, 17, 18, 23, 27, 48–56] the extraordinarily broadened component is accepted to be Gaussian Doppler due to a corresponding population of H with high kinetic energy [15, 17, 18, 23, 27–56].

Another possible mechanism involves charge accumulation and the development of a corresponding field in the plasma. Electrons impinge the alumina powder immersed in the plasmas, resulting in negative charge accumulation. The plasma potential that develops across the plasma is primarily a function of electron temperature T_e . For a thin plasma sheath domain wherein the plasma sheath is much smaller than the radius of the sphere (Alfa-Aesar: catalog number: 11711, 400 mesh powder; 37 μ , 99.9%), the plasma potential ϕ_a for a completely ionized hydrogen plasma is given by [63]:

$$\frac{e\phi_a}{\kappa T_e} = -\frac{1}{2} \ln \left(\frac{m_e}{m_i} \right) \approx -3.76 \quad (12)$$

where κ is the Boltzmann constant, and m_e and m_i are electron and ion masses, respectively.

In a recent study involving an Evenson cavity produced microwave plasma, S. Jovicevic et. al. [1] measured maximum $T_e \sim 0.15$ eV that corresponds to a sheath potential of ~ 0.58 V. Following the arguments of FAM, even if H⁺ ions get all the energy available by accelerating through this potential drop across the sheath, the resulting kinetic energy will be much less than 4 eV, the energy of excited n=3 state H atoms measured in this experiment. As a result, the observation of a fast H atom population far in excess of the electron temperature and the corresponding maximum sheath potential clearly demonstrates that an energy transfer process other than a field acceleration mechanism is responsible.

The fast component was assigned to resonance kinetic energy transfer during the hydrino transition reaction with the elimination of the only alternative mechanism, electric field acceleration, as the source of the energy of the extraordinarily fast H. The details of the transfer are given in Ref. [2]. The broadening increased in the static mode compared to the flow condition as predicted by the RTM wherein hydrinos increase with time to enhance the catalytic transition rate. As shown in Figures 3 and 5 for He/H₂ discharges and in Figures 6 and 7 for pure

H₂ plasmas, the fast population of H atoms in the excited (n=3) state (4 eV) was observed to increase from about ~20–25% to a significant portion of the Balmer α emission with time (50–60%) over a typical period of 1 hour at moderate microwave power levels of 20 W. In addition, a decrease in broadening with increasing concentrations of Xe in Xe/H₂ plasmas was observed. Only the RTM predicts this selectivity for fast H formation.

A further test of FAM was performed by studying the effect on the Balmer line widths with the application of a bias voltage to the 1%Pd/Al₂O₃. Figure 10 shows the results of the measurement of fast H atom energy as well as the fractional population for 50 mTorr hydrogen plasma at 40 W of microwave power as the biasing potential was varied from –250V to +250V. Contrary to FAM predictions, the H atom energy and fractional population in n=3 excited state remained independent of the biasing potential. Even though not shown, a similar observation was also made for H _{β} , H _{γ} and H _{δ} emission profiles.

III. Conclusion

In this study, we made specific theoretical predictions based on the RTM and tested them against FAMs, the competing theories for fast H, with standard easily interpretable experiments regarding the observation of fast H in microwave plasmas. Specifically, it is impossible according to FAM for fast H to be observed in hydrogen mixed gas microwave plasmas as unequivocally shown by Jovicevic et al. [1]. In contrast RTM predicts that fast H can be observed if the chemical conditions are present to support the reaction.

The fast H observation whose mechanism is controversial is but one signature of energetic hydrogen chemistry to form a new state of hydrogen that has been pursued in a separate field of investigation [2–27, 48–56, 64–68]. Other characteristic signatures of the reaction involving a resonant, nonradiative energy transfer from otherwise stable atomic hydrogen to the catalysts He^+ and $2H$ capable of accepting the energy to form hydrinos, $H(1/p)$, were observed and reported previously [15]. The catalyst energy transfer to pump the He^+ ion energy levels and increase the electron excitation temperature of H in helium-hydrogen and hydrogen plasmas was confirmed spectroscopically. In the former case, the pumping in the microwave plasma caused an inversion of the ion to atom line ratios, and in both cases, the $T_{excitation}$ was extraordinarily high, 2.5 eV to 3 eV, a factor of three increase over the typical temperature. For both catalysts, the energy due to the electron undergoing a radial transition to occupy a state of nearer radius was observed spectroscopically on pulsed DC plasmas as a characteristic EUV continuum with a cutoff at 228 Å and extending to longer wavelengths. It was also observed as third-body kinetic energy wherein a resonant kinetic energy transfer to form fast H was the source of extraordinary (>50 eV) Balmer α line broadening in DC and RF plasmas. The predicted molecular hydrino, $H_2(1/4)$, was observed at 1.25 ppm by solution NMR on gases collected from helium-hydrogen, water-vapor-assisted hydrogen, hydrogen, and strontium-argon-hydrogen rt-plasmas and dissolved in an NMR solvent. Thus, the experimental confirmation of all four predictions for transitions of atomic hydrogen to form hydrinos has been achieved on different plasma sources. These results are in good agreement with prior results on synthetic reactions to form hydrino compounds comprising hydrinos. The ¹H MAS NMR value of 1.13 ppm observed for $H_2(1/4)$ in solid $NaH * F$ corresponded to the solution value of 1.2 ppm and that of gases from plasma cells having a catalyst. The corresponding hydrino hydride ion $H^-(1/4)$ [2] was observed from solid compounds at the predicted shift of –3.86 ppm in

solution NMR and its ionization energy was confirmed at the predicted energy of 11 eV by X-ray photoelectron spectroscopy [17, 64–67].

It was anticipated that with sufficient enhancement of the reaction rate in microwave plasmas, the same fast H phenomenon observed in other plasma sources could be observed in microwave plasmas despite the unfavorably low electron temperature for excitation relative to fast-H cooling. A crucial test of energetic hydrogen chemistry regarding RTM versus FAM as the basis of this selective isotropic heating of a population of extraordinarily high-kinetic-energy hydrogen atoms is the observation of fast H in microwave cells proven to lack a high field as shown by the complete absence of fast H by Jovicevic et al. [1]. The RTM predicts an enhancement in the production of fast H with the presence of a surface to support a high concentration of hydrogen atoms in order to initiate the energetic hot-H source reaction that then propagates isotropically throughout the plasma. In contrast to the anticipated prior results, extraordinarily fast H of >4 eV and >50% population was observed as predicted for RTM using the catalytic reaction systems of He/H₂, Ar/H₂, pure H₂, and water vapor microwave plasmas as opposed to the non-catalytic Xe/H₂ system when a hydrogen-supporting material such as a commercial hydrogenation catalyst was placed in the plasma region. This reproduces prior results showing the fast H phenomenon in a system comprising an H-supporting surface wherein a floated thermocouple was present in the plasma to measure the neutral gas temperature [50, 51, 55, 68]. Further confirmation of a chemical source rather than an electric-field source of the fast H energy was provided by actually applying a high field. Contrary to FAM prediction, the H atom energies and fractional populations in n=3, 4, 5, and 6 excited states remained independent of a large range of biasing potential.

The power source of hot H being from the formation of hydrinos has implications for a commercial power source. The potential is already being realized as the power from the process has been independently confirmed at the 50 kW level [17, 64] with a thorough study by a team at Rowan University. Critic Rathke's issues [69, 70] regarding the application of classical laws with analytical solutions to atoms and molecules has similarly been dispatched in rebuttal publications [6, 71] and by the demonstration that the results are far advanced of the capabilities of nonphysical quantum mechanical theory [2–4] with its inherent weirdness, reliance on curve-fitting, and many inescapable failures [2–14].

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Figure 1. Schematic of the microwave plasma setup of a coaxial Evenson cavity inside a 0.5"×10" quartz tube.

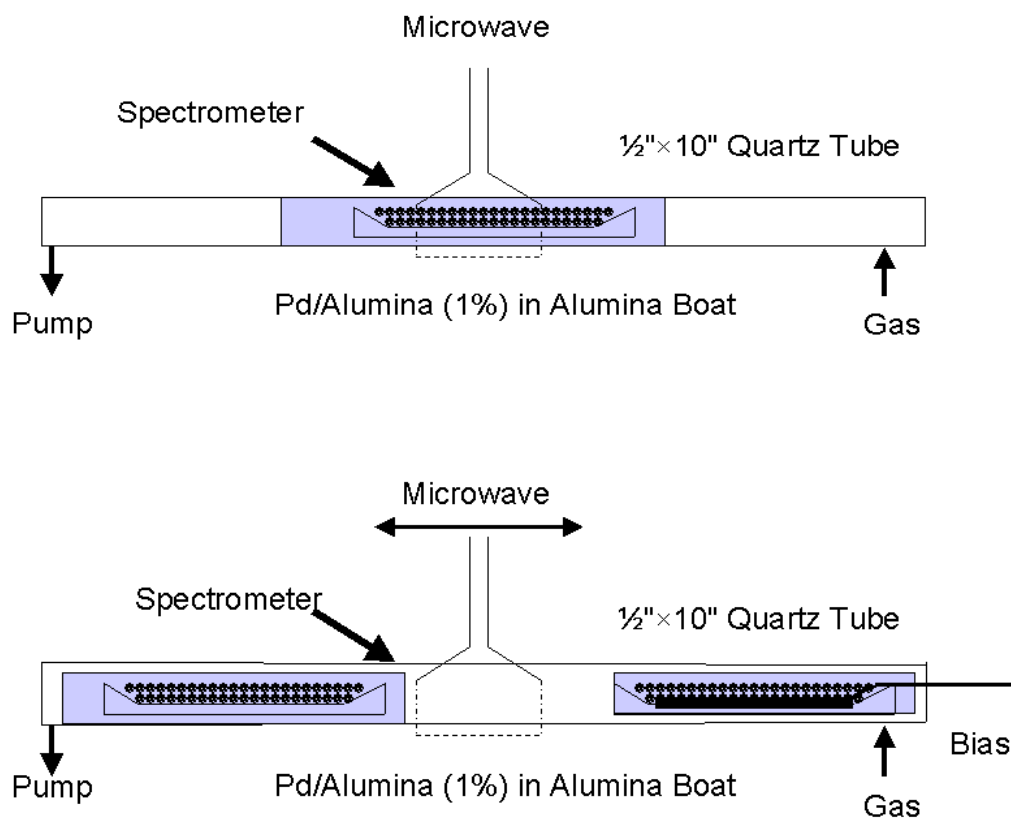


Figure 2. Balmer α emission profile of a 30 mTorr He/H₂ microwave discharge plasma with a net microwave power of 20 W having a Gaussian fit that yields a single temperature component with energy $\sim 0.1-0.2$ eV.

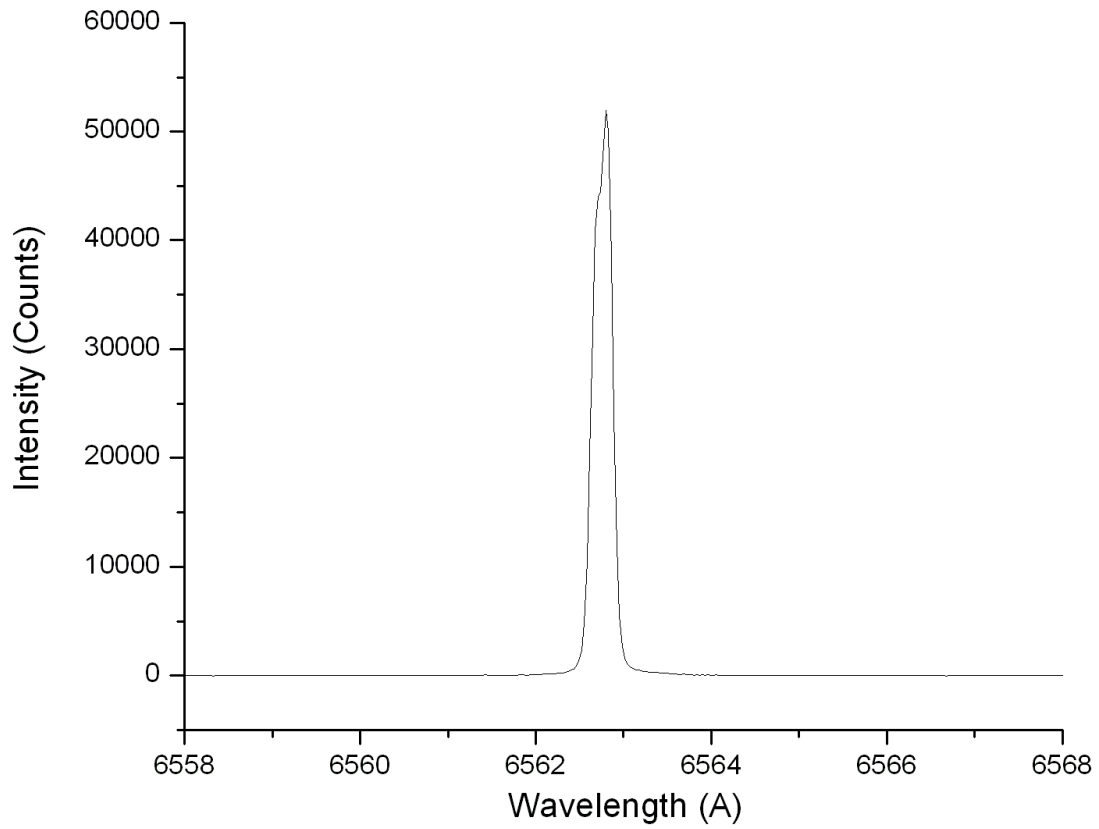
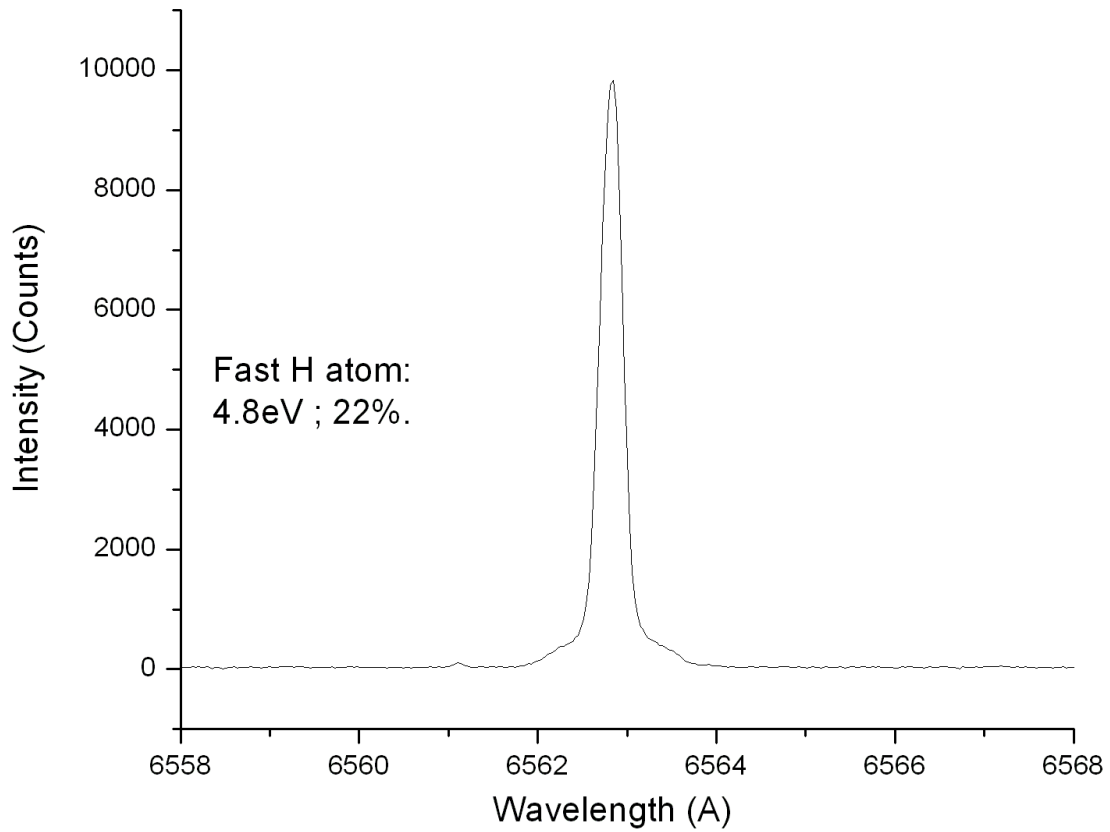


Figure 3. Balmer α emission profile when an alumina boat filled with 1% Pd/Al₂O₃ powder was placed under the microwave applicator to provide a surface to support hydrogen atoms. (a). An increase in the width of the Balmer α emission profile of 30 mTorr He/H₂ microwave discharge plasma was observed. (b). The curve is best fit by two Gaussians corresponding to two temperature populations of hydrogen atoms, one cold and one hot. In the latter case, the fast H atoms had an energy of ~ 4.8 eV and a fractional H atom population in the excited ($n=3$) state of 22%.

(a)



(b)

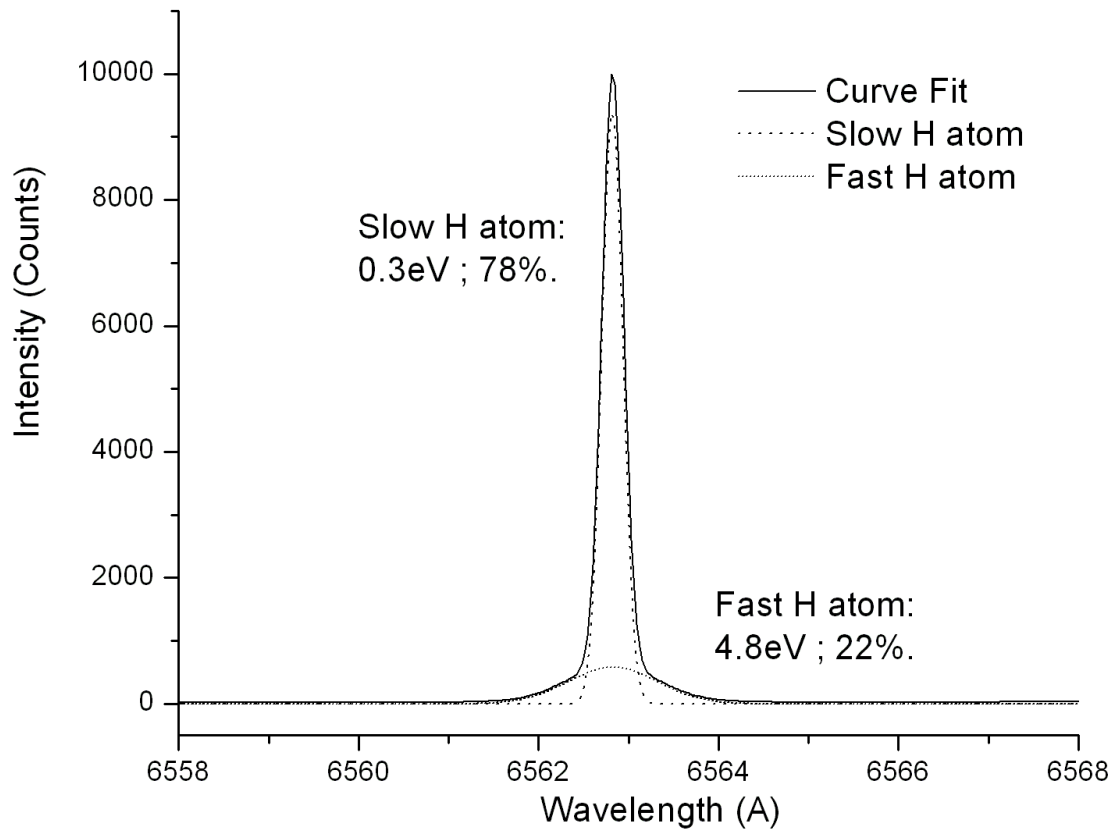


Figure 4. The Balmer α compared with the HeI emission profile for the 30 mTorr He/H₂ discharge in the flow mode with a net microwave power of 20W showing the absence of broadening of the HeI line; whereas, the Balmer α emission profile shows the presence of fast H atoms with an energy ~ 4.8 eV and a fractional population of fast H atoms in excited ($n=3$) state of 22%.

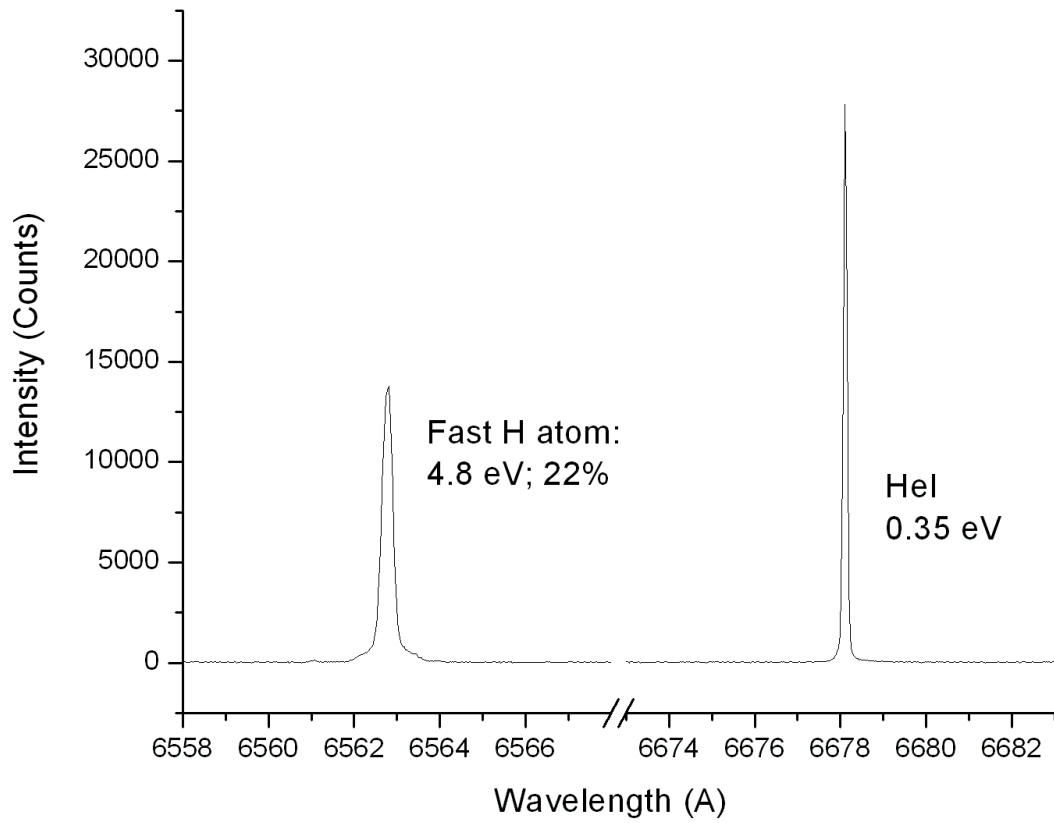


Figure 5. The Balmer α emission profile of a 30 mTorr He/H₂ microwave discharge plasma shows a very significant increase in the fractional population of fast H atoms in the excited (n=3) state to 63% with an energy of 2.83 eV in the batch mode wherein the vacuum pump was closed and the discharge was run for an hour.

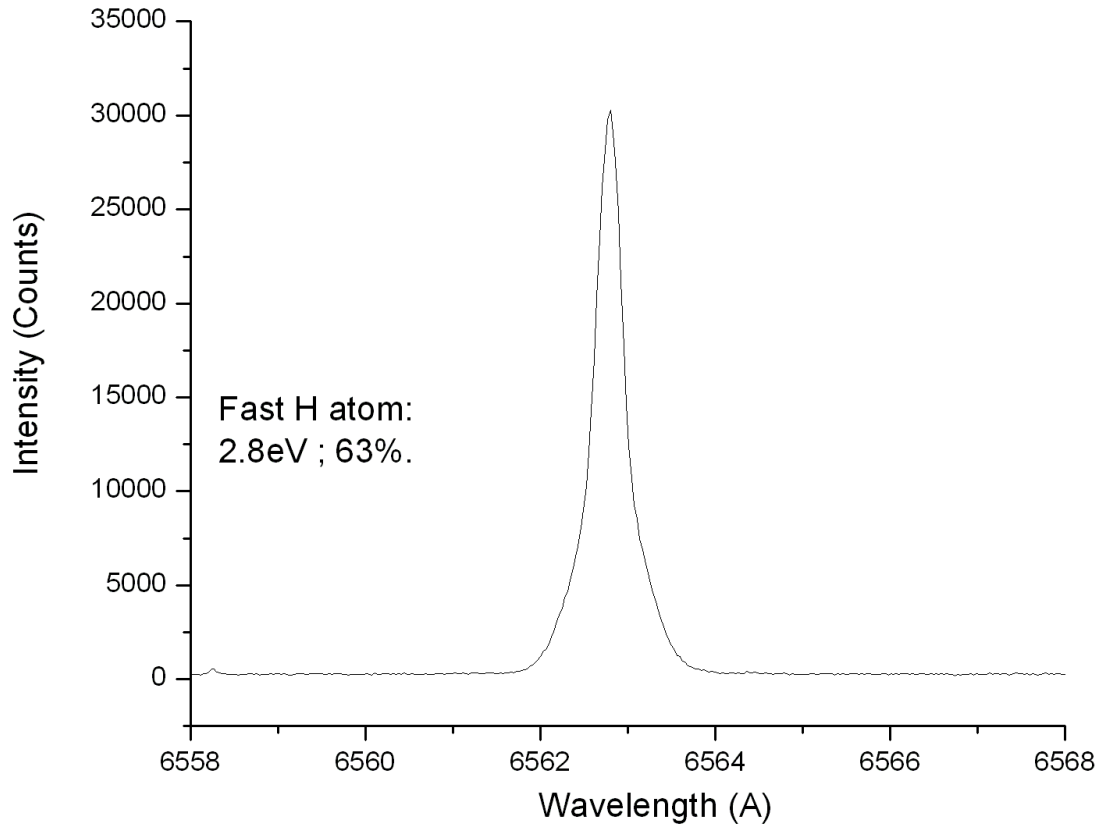


Figure 6. When an alumina boat filled with 1% Pd/Al₂O₃ powder was placed under the microwave applicator to provide a surface to support hydrogen atoms, an increase in the width of the Balmer α emission profile of 30 mTorr H₂ microwave discharge plasma was observed. A Gaussian fit shows fast H atoms with an energy of ~ 4.22 eV and a fractional H atom population in the excited (n=3) state of 25%.

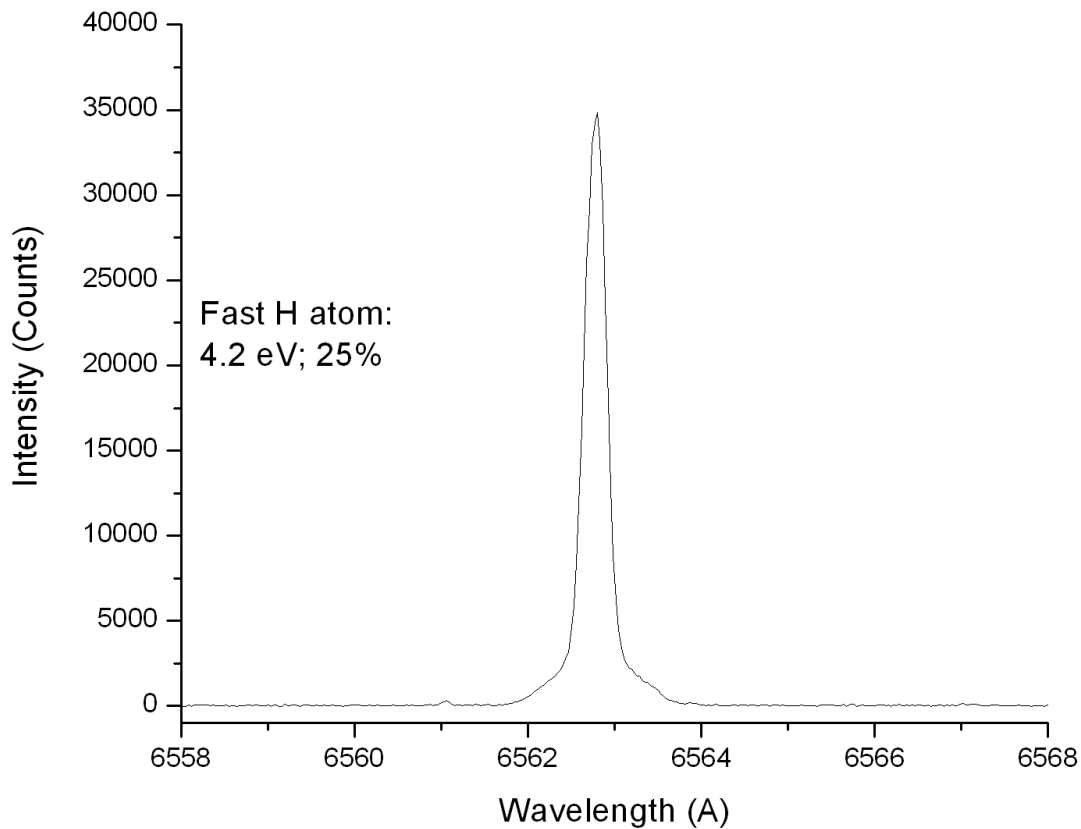


Figure 7. In the batch mode, the Balmer α emission profile of a 30 mTorr H_2 microwave discharge shows a very significant increase in the fractional population of fast H atoms in the excited ($n=3$) state to 52% with an energy of ~ 2.75 eV.

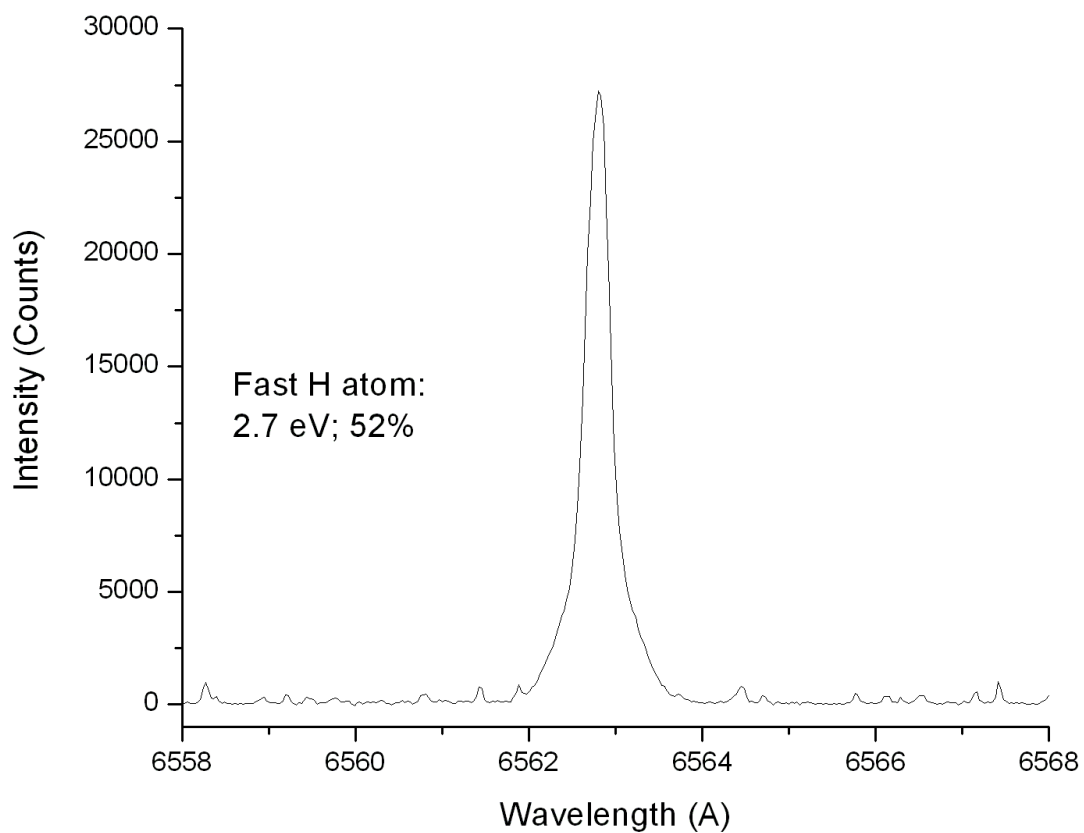


Figure 8. In the batch mode, the Balmer α emission profile of a 30 mTorr water vapor microwave plasma shows a very significant increase in the fractional population of fast H atoms in the excited ($n=3$) state to 62% with an energy of ~ 2.7 eV.

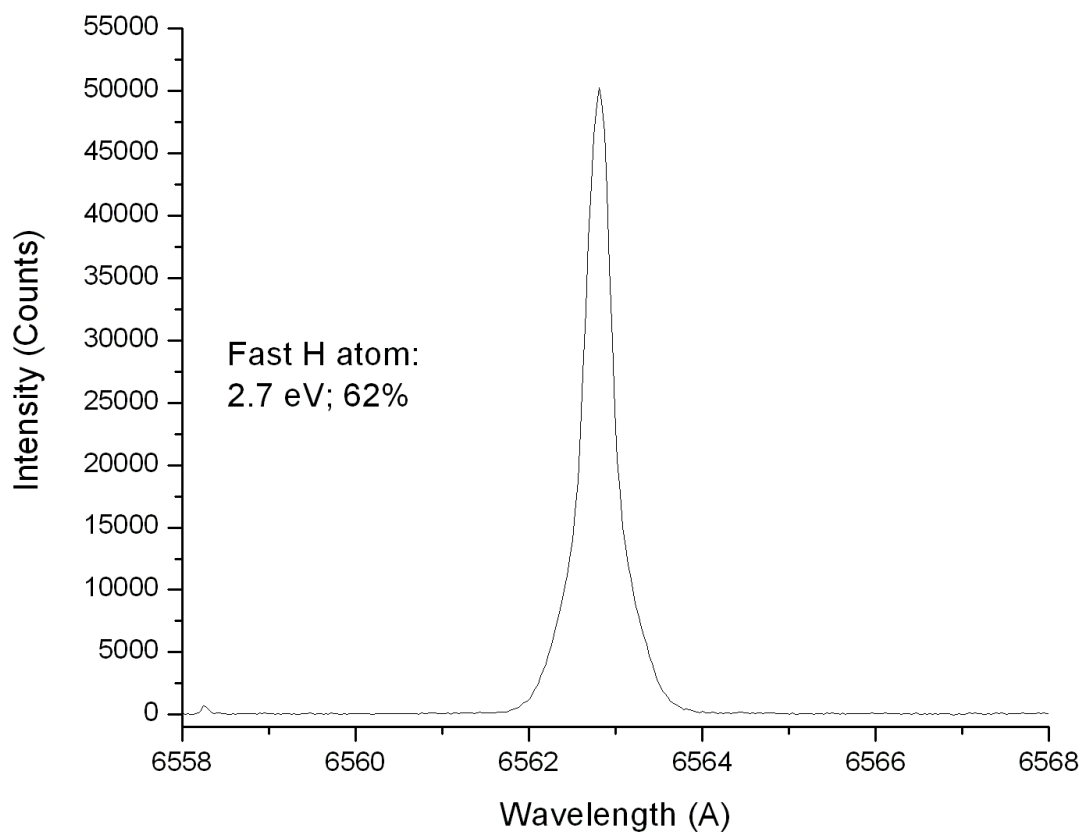


Figure 9. Running each in the batch mode and at 50% hydrogen content, the normalized Balmer α emission profiles of Xe/H₂ compared to He/H₂ discharges at 30 mTorr showed a dramatic reduction in fast H with the substitution of Xe for He. From the Doppler width of the Gaussian profile, the energy and fractional population of fast H atoms in the excited ($n=3$) state for the Xe/H₂ discharge were 1.4 eV and 8%, respectively. In contrast, these parameters for the He/H₂ discharge were 2.83 eV and 63%, respectively.

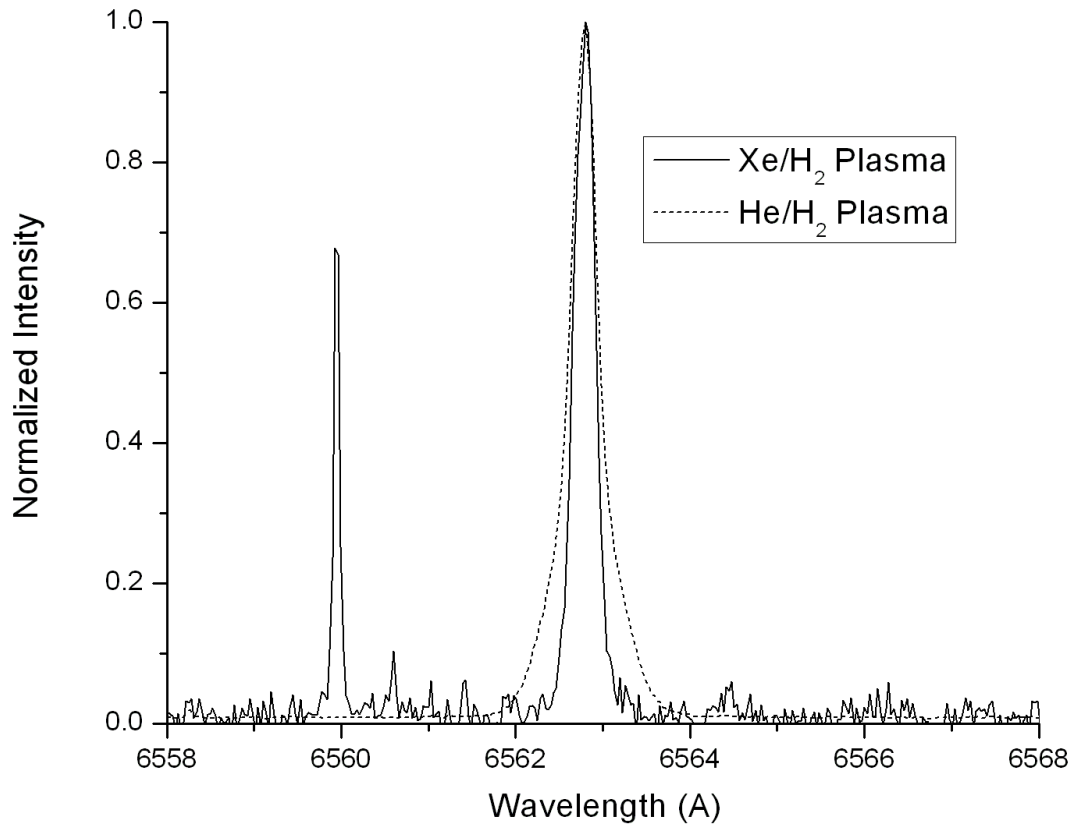


Figure 10. Fast H atom energy and fractional population in the excited $n=3$ state as a function of biasing potential in a 50 mTorr hydrogen plasma at 40 W of microwave power. The applied high field had no effect in contradiction to the predictions of FAM.

