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Substantial changes in the characteristics of a microwave plasma due to combining argon and hydrogen

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Abstract. Upon the addition of 5% argon to a hydrogen plasma, the Lyman α emission was observed to increase by about an order of magnitude, whereas xenon control had no effect. With a microwave input power of 40 W, the gas temperature of an argon plasma increased from 400 to over 750 °C with the addition of 3% flowing hydrogen, whereas the 400 °C temperature of a xenon plasma run under identical conditions was essentially unchanged with the addition of hydrogen. The average hydrogen-atom temperature of the argon–hydrogen plasma was measured to be 110–130 eV versus ≈ 3 eV for pure hydrogen or xenon–hydrogen. Mechanisms such as Stark broadening or acceleration of charged species due to high fields (e.g. over 10 kV cm⁻¹) cannot be invoked to explain the results with argon since the electron density was low and no high field was observationally present. The electron temperature T_e for the argon–hydrogen and xenon–hydrogen plasmas was $11\,600 \pm 5\%$ and $6500 \pm 5\%$ K, respectively, compared to $4800 \pm 5\%$ and $4980 \pm 5\%$ K for argon and xenon alone, respectively. The observation of higher temperatures corresponding to three possibly independent plasma parameters for only argon with hydrogen may be explained by the release of energy from atomic hydrogen by a resonant nonradiative energy-transfer mechanism.

1. Introduction

It was reported previously that a new plasma source has been developed that operates by incandescently heating a hydrogen dissociator to provide atomic hydrogen and heats a catalyst such that it becomes gaseous and reacts with the atomic hydrogen to produce a plasma called a resonance-transfer or rt-plasma. It was extraordinary that intense VUV emission was observed by

Mills *et al* [1, 2] at low temperatures (e.g. $\approx 10^3$ K) and an extraordinary low field strength of about $1\text{--}2\text{ V cm}^{-1}$ from atomic hydrogen and certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV.

Prior related studies that support the possibility of a novel reaction of atomic hydrogen which produces a chemically generated or assisted plasma (rt-plasma) and produces novel hydride compounds include EUV spectroscopy [1]–[12, 14], characteristic emission from catalysts and the hydride-ion products [8]–[11], lower-energy hydrogen emission [3]–[5, 7], chemically formed plasmas [1, 2, 6, 8]–[12], Balmer α line broadening [3]–[5, 11, 13, 15], elevated electron temperature [3, 5, 13], anomalous plasma afterglow duration [6, 14], power generation [2, 3, 12, 15, 16], and analysis of novel chemical compounds [17]. Argon ions can provide a net enthalpy of a multiple of that of the potential energy of the hydrogen atom. The second ionization energy of argon is 27.63 eV [18]. The reaction $\text{Ar}^+ - \text{Ar}^{2+}$ has a net enthalpy of reaction of 27.63 eV. Thus, an argon microwave discharge with hydrogen present was anticipated to form an rt-plasma, and the effect of the addition of hydrogen to an argon microwave plasma compared to xenon control was determined. The plasmas were characterized by measuring the plasma gas temperature, the average hydrogen-atom temperature and number density from Balmer α line broadening, and the electron temperature T_e from intensity ratios of the Ar 104.8 nm and Ar 420.06 nm lines.

2. Experimental details

The experimental set-up comprising a microwave discharge gas cell light source and an EUV spectrometer which was differentially pumped is shown in figure 1. Extreme ultraviolet emission spectra were obtained on plasmas of hydrogen alone, hydrogen–argon mixture (95/5%), and hydrogen–xenon mixture (95/5%). Hydrogen or the hydrogen–noble-gas mixture was caused to flow through a half-inch-diameter quartz tube at 1 Torr that was maintained by causing the hydrogen or the gas mixture to flow while monitoring the pressure with a 10 and 1000 Torr MKS Baratron absolute pressure gauge. The tube was fitted with an Opthos coaxial microwave cavity (Evenson cavity). The microwave generator shown in figure 1 was an Opthos model MPG-4M generator (frequency: 2450 MHz). The power input to the plasma was set at 85 W.

For spectral measurement, the light emissions from the microwave plasmas were introduced to a normal-incidence McPherson 0.2 m monochromator (Model 302, Seya–Namioka type) equipped with a 1200 lines mm^{-1} holographic grating with a platinum coating. The wavelength region covered by the monochromator was 5–560 nm. The UV spectrum (90–165 nm) of the cell emission was recorded with a channel electron multiplier (CEM). The wavelength resolution was about 1 nm (FWHM) with an entrance and exit slit widths of 300 μm . The increment was 0.2 nm and the dwell time was 500 ms.

In order to estimate the relative power output [19], the gas temperatures of the microwave plasmas of argon and xenon alone and each noble gas with 10% hydrogen were measured. Each ultrapure test gas or mixture was caused to flow through the half-inch-diameter quartz tube at 0.3 Torr maintained with a noble-gas flow rate of 9.3 sccm or a noble-gas flow rate of 8.3 sccm and a hydrogen flow rate of 1 sccm.

With the input power to the plasma set at 40 W, the temperature rise and fall were recorded using a K-type thermocouple (± 0.1 °C) housed in a stainless steel tube that was placed axially inside the centre of the 10 cm^3 plasma volume of a quartz microwave cell as hydrogen flow supplied by the mass flow controller was turned on and off. The ambient temperature was

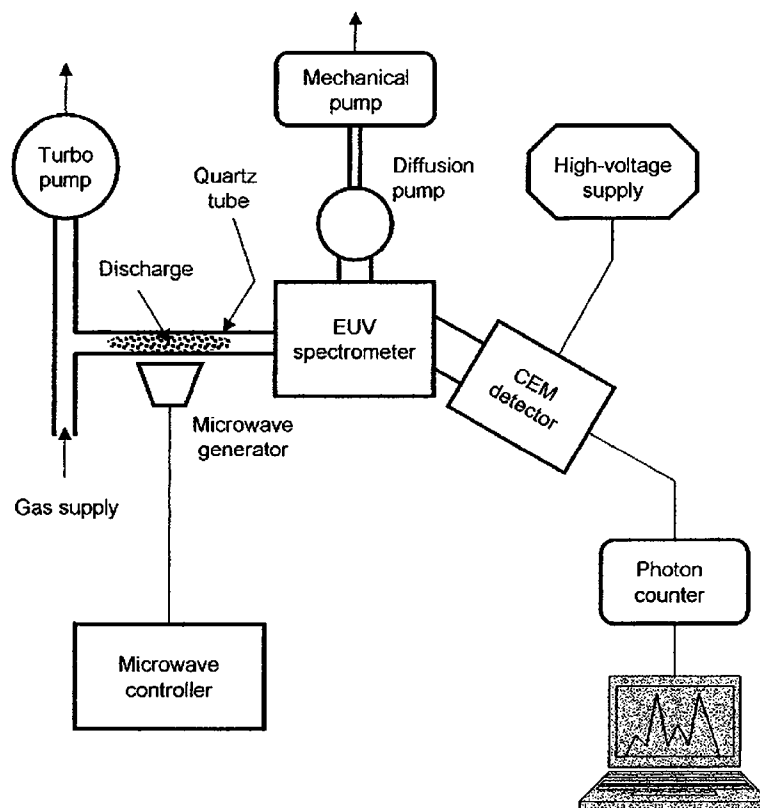


Figure 1. The experimental set-up comprising a microwave discharge gas cell light source and an EUV spectrometer which was differentially pumped.

$25 \pm 0.1^\circ\text{C}$. The cell was operated under flow conditions with continuous pumping by the turbopump of the EUV spectrometer.

Balmer α emission from the cell was also recorded with a high-resolution visible spectrometer to determine the energy and density. The method of Videnovic *et al* [20] was used to calculate the energetic hydrogen-atom densities and energies from the width of the 656.3 nm Balmer α line emitted from glow discharge and microwave plasmas. The full half-width $\Delta\lambda_G$ of each Gaussian results from the Doppler ($\Delta\lambda_D$) and instrumental ($\Delta\lambda_I$) half-widths:

$$\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2}. \quad (1)$$

$\Delta\lambda_I$ in our experiments was 0.006 nm. The temperature was calculated from the Doppler half-width using the formula

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

where λ_0 is the line wavelength in nm, T is the temperature in K (1 eV = 11 605 K), and μ is the molecular weight (=1 for hydrogen). In each case, the average Doppler half-width that was not appreciably changed with pressure varied by $\pm 5\%$ corresponding to an error in the energy of $\pm 5\%$. The corresponding number densities for noble-gas-hydrogen mixtures varied by $\pm 20\%$ depending on the pressure. The spectra were taken ten times per experiment and were found to be reproducible within less than $\pm 5\%$.

The width of the 656.3 nm Balmer α line was measured using light emitted from microwave discharges of pure hydrogen alone and a mixture of 10% hydrogen and argon or xenon. The plasma emission was fibre-optically coupled through a 220F matching fibre adapter positioned 2 cm from the cell wall to a high-resolution visible spectrometer with a resolution of ± 0.006 nm over the spectral range 190–860 nm. The spectrometer was a Jobin-Yvon Horiba 1250 M with a 2400 grooves mm^{-1} ion-etched holographic diffraction grating. The entrance and exit slits were set to 20 μm . The spectrometer was scanned between 655.5 and 657 nm using a 0.005 nm step size. The signal was recorded by a PMT with a stand-alone high-voltage power supply (950 V) and an acquisition controller. The data were obtained in a single accumulation with a 1 s integration time.

The spectroscopic diagnostic method most commonly used to determine the electron temperature T_e of laboratory plasmas is based on determining the relative intensities of two spectral lines as described by Griem [21]. It may be shown that, for two emission lines at wavelengths λ_A and λ_B ,

$$\frac{I_A}{I_B} = \frac{(\sigma g_2 A_{21})_A}{(\sigma g_2 A_{21})_B} \exp\left(-\frac{(E_{2A} - E_{2B})}{kT_e}\right) \quad (3)$$

where I_A and I_B are the intensities measured at λ_A and λ_B , and $\sigma \propto n^4$ for atomic hydrogen where n is the principal quantum number. The frequency ν , the transition probability A , the degeneracy g , and the upper level E are known constants from which T_e was determined.

T_e was measured for microwave plasmas of argon alone and argon–hydrogen mixture (90/10%) from the ratio of the intensity of the Ar 104.8 nm (upper quantum level $n = 3$) line to that of the Ar 420.06 nm ($n = 4$) line. T_e was also measured by the same method for microwave plasmas of pure hydrogen alone, xenon alone, and a mixture of 10% hydrogen and xenon using the ratio of the intensities of two hydrogen or xenon lines in two quantum states. The spectra were repeated five times per experiment and were found to be reproducible within less than $\pm 5\%$.

The electron density was determined according to the method given previously [22].

3. Results and discussion

3.1. Argon–hydrogen microwave emission spectrum

The EUV spectra (90–165 nm) of the cell emission from the hydrogen plasma (dotted curve) and the hydrogen plasma to which 5% argon was added (solid curve) are shown in figure 2. Upon the addition of 5% argon, the hydrogen Lyman α emission intensity was observed to increase by about an order of magnitude. Essentially no effect was observed for the addition of 5% xenon to the hydrogen plasma. This result indicates that one or more temperatures may be elevated with the addition of argon to a hydrogen plasma.

3.2. Gas temperature measurements and estimation of the power balance

The origin of Doppler broadening is the relative thermal motion of the emitter with respect to the observer—in this case the spectrometer. Since it was very high, and no conventional explanation was found, the rt-plasma must have a source of free energy. To determine an estimate of the power of the underlying chemical reaction, the gas temperature was measured with the addition and removal of hydrogen as compared to a control plasma.

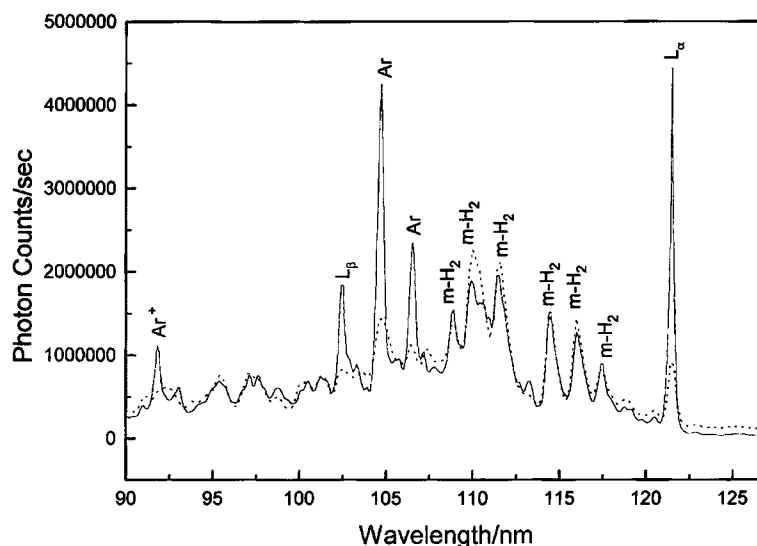


Figure 2. The EUV spectra (90–165 nm) of the cell emission from the hydrogen plasma (dotted curve) and the hydrogen plasma to which 5% argon was added (solid curve).

Due to the high mobility of free electrons, the heat loss of the microwave cell was determined by slow losses from the cell walls with a fast power transfer from the plasma to the wall. In this case, the plasma was isothermal and the inner wall temperature and the plasma gas temperatures were equivalent, as discussed by Chen *et al* [19]. Since the microwave discharge cell, power input to the plasma, and discharge conditions remained identical between the argon and xenon experiments, the gas temperature of the cell may be used to determine the power balance. At steady state, the power P_T lost from the cell was equal to the power supplied to the cell P_{in} plus any excess power P_{ex} :

$$P_T = P_{in} + P_{ex}. \quad (4)$$

Since the heat transfer was dominated by conduction from the outer cell walls, the temperature rise of the cell above ambient ΔT was modelled by the following relationship:

$$\Delta T = aP_T \quad (5)$$

where a is a constant for the cell temperature response to power input for the control experiments ($P_{ex} = 0$). ΔT was recorded for $P_{in} = 40$ W for argon alone, noncatalyst xenon alone, and xenon with the addition of hydrogen. The higher temperature produced by the argon with the addition of hydrogen compared with the control gases was representative of the excess power. In the case of the catalyst run, the total output power P_T was determined by solving equation (5) using the measured ΔT . The excess power P_{ex} was determined from equation (4).

Essentially no increase in gas temperature was observed with the addition of hydrogen to the xenon control as shown in figure 3. In contrast, with a microwave input power of 40 W, the gas temperature of an argon plasma increased from 400 to 785 °C with the addition of 3% flowing hydrogen as shown in figure 4. Using the average temperature increase above the ambient temperature, $\Delta T = 425 - 25 = 400$ °C, and the input power, $P_{in} = 40$ W, applied to each of the control plasmas to solve for a in equation (5) gives

$$\Delta T = 10 \times P_T \quad (6)$$

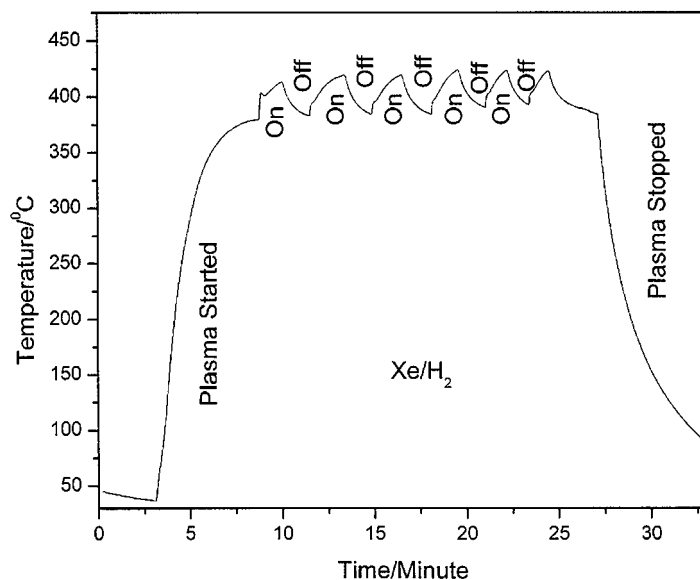


Figure 3. The plasma gas temperature rise as a function of time for xenon alone and the xenon–hydrogen mixture (90/10%) with the microwave input power set at 40 W as the hydrogen flow was turned on and off. The 400 °C plasma gas temperature was essentially unchanged with the addition of hydrogen.

where ΔT is in °C and P_T is in watts. Thus, with a microwave input power of 40 W, the thermal output power was estimated using equation (6) to be 76 W. From equation (4), the excess power was 36 W. Since the hydrogen flow rate was 1 sccm, an estimate of the corresponding energy balance was over $-1 \times 10^4 \text{ kJ (mol H}_2\text{)}^{-1}$ compared to the enthalpy of combustion of hydrogen of $-241.8 \text{ kJ (mol H}_2\text{)}^{-1}$.

3.3. Line broadening and T_e -measurements

The 656.3 nm Balmer α linewidths recorded with a high-resolution ($\pm 0.006 \text{ nm}$) visible spectrometer for microwave discharge plasmas of hydrogen compared with those for xenon–hydrogen (90/10%) and argon–hydrogen (90/10%) are shown in figures 5 and 6, respectively. The statistical curve fit of the hydrogen plasma and the argon–hydrogen plasma emission are shown in figures 7 and 8, respectively. In each case, the data matched a Gaussian profile having the χ^2 - and R -values given in figures 7 and 8. The energetic hydrogen-atom densities and energies of plasmas of hydrogen alone and the noble-gas–hydrogen mixtures were calculated using the method of Videnovic *et al* [20]. It was found that the microwave argon–hydrogen plasma showed extraordinary broadening corresponding to an average hydrogen-atom temperature of 110–130 eV and an atom density of $3.5 \times 10^{14} \text{ atoms cm}^{-3}$, whereas xenon–hydrogen and pure hydrogen showed no excessive broadening corresponding to an average hydrogen-atom temperature of 3–4 eV for both and atom densities of only 3×10^{13} and $7 \times 10^{13} \text{ atoms cm}^{-3}$, respectively, even though ten times more hydrogen was present for pure hydrogen.

Similarly to the hydrogen-atom temperature, the average electron temperature T_e for the argon–hydrogen plasma was high, $11\,600 \pm 5\%$, compared to 4800 ± 5 , 4980 ± 5 , and $6500 \pm 5\%$ K for argon alone, xenon alone, and xenon–hydrogen plasmas, respectively.

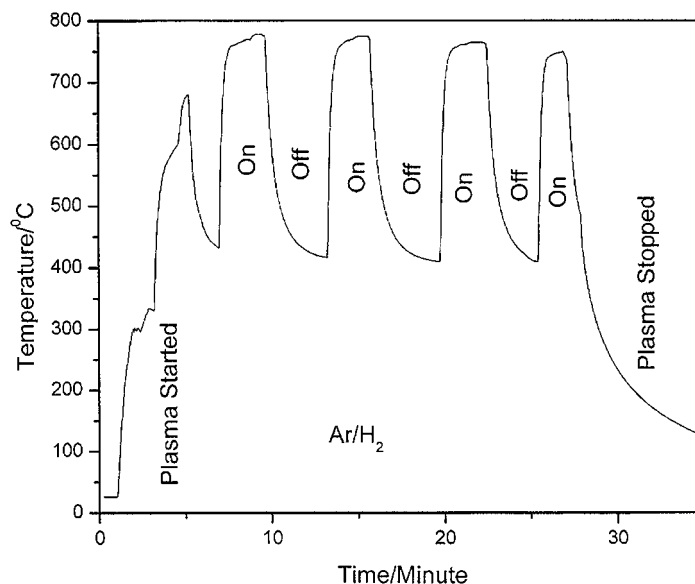


Figure 4. The plasma gas temperature rise as a function of time for argon alone and the argon–hydrogen mixture (90/10%) with the microwave input power set at 40 W as the hydrogen flow was turned on and off. The plasma gas temperature reproducibly increased from 400 °C to over 750 °C with the addition of 3% flowing hydrogen. The thermal output power of the argon–hydrogen plasma was estimated to be 76 W.

We have assumed that Doppler broadening due to thermal motion was the dominant source to the extent that other sources may be neglected. To confirm this assumption, each source is now considered. In general, the experimental profile is a convolution of two Doppler profiles, an instrumental profile, the natural (lifetime) profile, Stark profiles, van der Waals profiles, a resonance profile, and fine structure. The instrumental half-width is measured to be ± 0.006 nm. The natural half-width of the Balmer α line given by Djurovic and Roberts [23] is 1.4×10^{-4} nm which is negligible. The fine-structure splitting is also negligible.

With conventional emission or absorption spectroscopy, Stark broadening of hydrogen lines in plasmas cannot be measured at low electron densities because it is hidden by Doppler broadening. For the Lyman α line, the Stark width is larger than the Doppler width only at $n_e > 10^{17}$ cm $^{-3}$ for temperatures of about 10^4 K [24].

The relationship between the Stark broadening $\Delta\lambda_S$ of the Balmer β line in nm, the electron density n_e in m $^{-3}$, and the electron temperature T_e in K is

$$\log n_e = C_0 + C_1 \log(\Delta\lambda_S) + C_2 [\log(\Delta\lambda_S)]^2 + C_3 \log(T_e) \quad (7)$$

where $C_0 = 22.578$, $C_1 = 1.478$, $C_2 = -0.144$, and $C_3 = 0.1265$ [25]. From equation (7), to get a Stark broadening of only 0.1 nm with $T_e = 9000$ K, an electron density of about $n_e \sim 3 \times 10^{15}$ cm $^{-3}$ is required compared to that of the argon–hydrogen plasma of $n_e < 10^{10}$ cm $^{-3}$ determined using a Langmuir probe, over five orders of magnitude less. Gigoso and Cardenoso [26] give the observed Balmer α Stark broadening for plasmas of hydrogen with helium or argon as a function of the electron temperature and density. For example, the Stark broadening of the Balmer α line recorded on a H + He $^+$ plasma is only 0.033 nm with

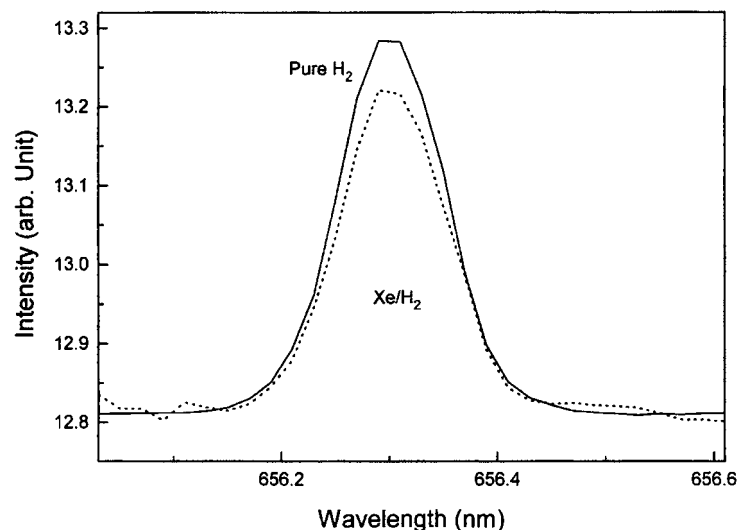


Figure 5. The 656.3 nm Balmer α linewidth recorded with a high-resolution (± 0.006 nm) visible spectrometer for a xenon–hydrogen (90/10%) and a hydrogen microwave discharge plasma. No excessive line broadening was observed corresponding to an average hydrogen-atom temperature of 3–4 eV.

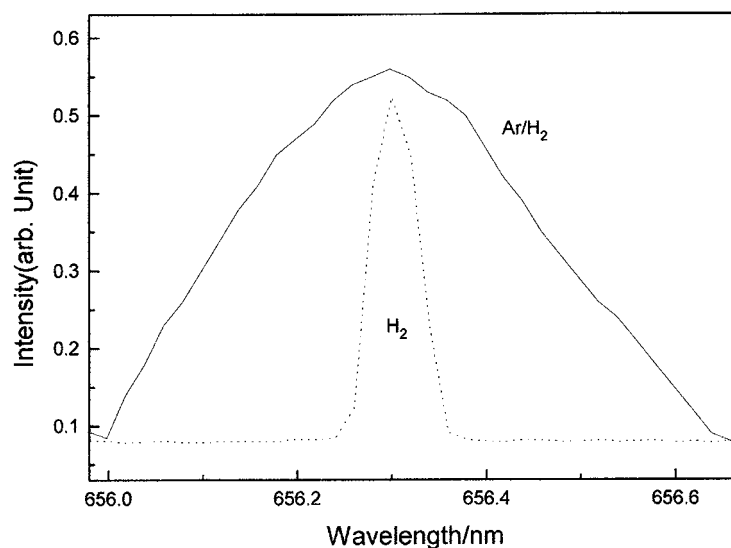


Figure 6. The 656.3 nm Balmer α linewidth recorded with a high-resolution (± 0.006 nm) visible spectrometer for a argon–hydrogen (90/10%) and a hydrogen microwave discharge plasma. Significant broadening was observed corresponding to an average hydrogen-atom temperature of 110–130 eV.

$T_e = 20\,000$ K and $n_e = 1.4 \times 10^{14}$ cm $^{-3}$. Thus, the Stark broadening was also insignificant. This result was also evident in the good fit to a Gaussian profile rather than a Voigt profile as shown in figure 8.

A linear Stark effect arises from an applied electric field that splits the energy level with principal quantum number n into $(2n - 1)$ equidistant sublevels. The magnitude of this effect

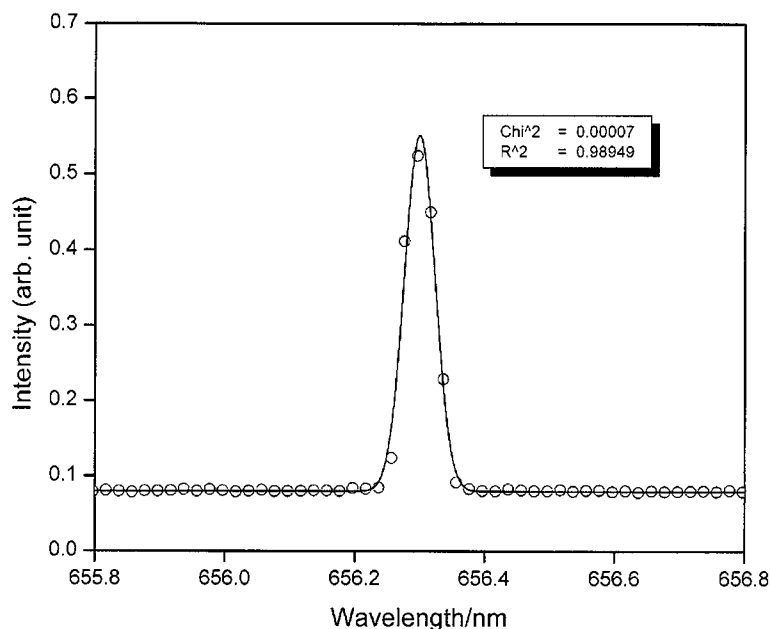


Figure 7. The statistical curve fit of the hydrogen plasma. The data matched a Gaussian profile having the χ^2 - and R -values of 0.00007 and 0.98949, respectively.

given by Videnovic *et al* [20] is about $2 \times 10^{-2} \text{ nm kV}^{-1} \text{ cm}^{-1}$. No applied electric field was present in our study; thus, the linear Stark effect should be negligible.

To investigate whether the rt-plasmas of this study were optically thin or thick at a given frequency ω , the effective path length $\tau_\omega(L)$ was calculated from

$$\tau_\omega(L) = \kappa_\omega L \quad (8)$$

where L is the path length and κ_ω is the absorption coefficient given by

$$\kappa_\omega = \sigma_\omega \chi N_H \quad (9)$$

where σ_ω is the absorption cross section and N_H is the number density of the absorber. For optically thin plasmas $\tau_\omega(L) < 1$, and for optically thick plasmas $\tau_\omega(L) > 1$. The absorption cross section for Balmer α emission is $\sigma = 8 \times 10^{-19} \text{ cm}^2$ [27, 28, 29]. As discussed above, an estimate based on emission line profiles places the total H-atom density at $\sim 3.5 \times 10^{14} \text{ cm}^{-3}$. Since this is overwhelmingly dominated by the ground state, $N_H = 3.5 \times 10^{14} \text{ cm}^{-3}$ will be used. Thus, for a plasma length of 5 cm, $\tau_\omega(5 \text{ cm})$ for Balmer α is

$$\tau_\omega(5 \text{ cm}) = \kappa_\omega L = (8 \times 10^{-19} \text{ cm}^2)(3.5 \times 10^{14} \text{ cm}^{-3})(5 \text{ cm}) = 1.4 \times 10^{-3}. \quad (10)$$

Since $\tau_\omega(5) \ll 1$, the argon–hydrogen plasmas were optically thin; so, the self-absorption of 656.3 nm emission by $n = 1$ state atomic hydrogen may be neglected as a source of the observed broadening.

Usually, the atomic hydrogen collisional cross section in plasmas is of the order of 10^{-18} cm^2 [30]. Thus, for $N_H = 3.5 \times 10^{14} \text{ cm}^{-3}$, collisional or pressure broadening is negligible.

A number of mechanisms have been proposed in order to explain the excessive Doppler broadening of the Balmer α line in argon–hydrogen DC- or rf-driven glow discharge plasmas.

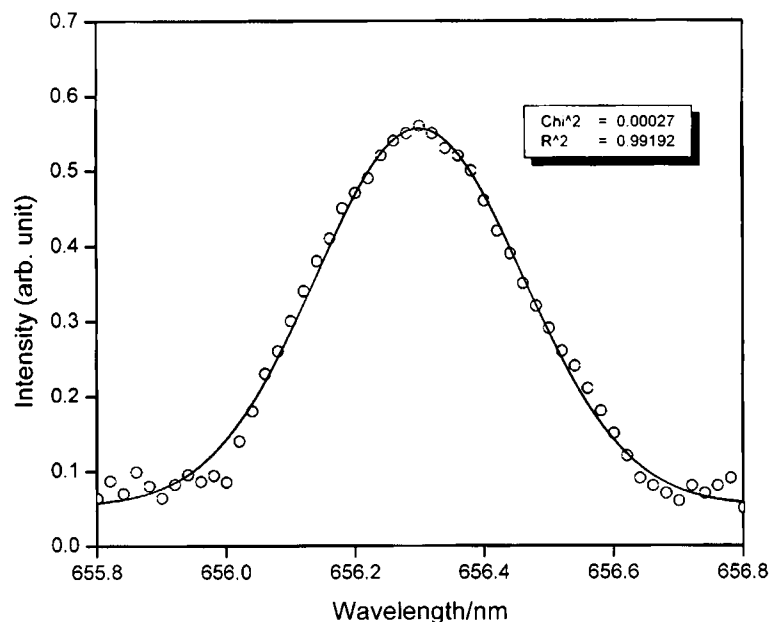


Figure 8. The statistical curve fit of the argon–hydrogen plasma. The data matched a Gaussian profile having the χ^2 - and R -values of 0.000 27 and 0.991 92, respectively.

Many of these have subsequently been shown to be untenable on the basis of additional data of others or our results with microwave plasmas where no applied field is present. For example, Kuraica and Konjevic [31] observed 50 eV anomalous thermal broadening of the Balmer lines during plane-cathode abnormal glow discharges of hydrogen–argon mixtures which was not observed with neon–hydrogen mixtures or pure hydrogen irrespective of the cathode material—copper, carbon, or silver. To explain the excessive broadening with the presence of argon, they proposed the quiresonant charge-transfer process



with the further reaction



occurring to a significant extent due to its large cross section. The authors state:

‘However, in either case, it is essential that 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/atom) cannot be explained’.

In our experiments, the 110–130 eV line broadening observed for an argon–hydrogen microwave plasma cannot be explained by this mechanism since no external field was present. In addition, broadening for argon–hydrogen plasmas cannot be explained purely by a resonance energy transfer to H_2^+ which is accelerated in the electric field to dissociate as energetic atomic hydrogen as proposed by Kuraica and Konjevic [31]. 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. This 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.

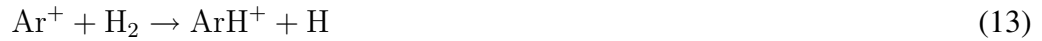
Djurovic and Roberts [23] recorded the spectral and spatial profiles of Balmer α line emission from low-pressure rf (13.56 MHz) discharges in $\text{H}_2 + \text{Ar}$ mixtures in a direction normal to the electric field. The introduction of Ar in a pure H_2 plasma increased the number of fast neutral 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 temperature of a wide profile component was 23.8 eV for voltages above 100 V, and the average temperature 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 temperature 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 which 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 $^{-1}$. Thus, the distance travelled must be less than 0.001 m.

The experimental evidence from several sources including ours does not support this mechanism.

- (1) Only the number, but not the average energy (23.8 eV), of fast H excited atoms was observed to be dependent on the position between the electrodes and the pressure for the same peak-to-peak voltage (200 V). For a mechanism based on acceleration of any charged species in a special region such as the cathode fall region, this is unexpected.
- (2) Since the measurements were taken perpendicular to the applied electric field, the symmetrical Doppler shape of both components centred at the same wavelength indicated that there were no directional velocity effects from the applied electric field. 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 atoms in the red wing due to fast motion toward the powered electrode arise from accelerated H_2^+ , whereas those 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^+ or fast H_2 . Momentum transfer must occur at the electrode and gaps and/or asymmetries in the intensity would be expected for the 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.
- (3) Radovanov *et al* [32] studied the excited neutrals and fast ions produced in a 13.56 MHz radio-frequency discharge in a 90% argon–10% hydrogen gas mixture by spatially and temporally resolved optical emission spectroscopy and by mass-resolved measurements of ion kinetic energy distributions at the grounded electrode. They concluded that a significant contribution of fast H atoms from H_2^+ is unlikely, due to the very fast conversion of H_2^+ to H_3^+ . They determined that H_3^+ was the dominant light ion with H^+ and H_2^+ having intensities at least ten times lower. In addition, H_3^+ had the highest mean energy of the ions, even though H^+ exhibited the highest maximum kinetic energies. From these results, they concluded that H_3^+ rather than H_2^+ was the primary source of fast H emitted from the surface of the powered electrode.

- (4) The Djurovic and Roberts mechanism of the excessive broadening caused by the addition of argon does not explain the lack of an effect with neon as shown by Kuraica and Konjevic [31]. Nor does it explain the lack of an effect with xenon in this study or the greater effect with helium in previous studies [13].
- (5) All prior mechanisms used to explain the excessive Balmer α line broadening in argon–hydrogen plasmas are based on the absolute requirement of an electric field which is absent in our microwave plasma experiments.

Videnovic *et al* [20] 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^+ [19]. And, according to Bogaerts and Gijbels [27], H_3^+ is the dominant hydrogen ion in argon–hydrogen plasmas due to the rapid reaction of H_2^+ with H_2 . Videnovic *et al* [20] claim the production of significant amounts of H_3^+ by participation of the argon ion through reactions such as



However, Bogaerts and Gijbels [27] show that protonated argon is rapidly reduced by electrons. The reaction



has a high rate constant of $k \sim 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ [27], whereas the formation of ArH^+ is much slower. The rate constant and cross section for proton transfer given by equation (13) are $k \sim 4 \times 10^{-10} - 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and $\sigma \sim 2 \times 10^{-15} \text{ cm}^2$, respectively [27], which are not favourable. Similarly, the rate constant and cross section for charge transfer given by



are $k \sim 2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $\sigma \sim 10^{-15} \text{ cm}^2$, respectively [27]. These reactions are very unlikely to contribute to the production of H_3^+ in an appreciable manner since the degree of ionization of argon is typically low, $10^{-5} - 10^{-4}$ [27]. And Ar actually contributes to the destruction of H_3^+ through the reaction



which has a significant cross section of $\sigma \sim 5 \times 10^{-16} \text{ cm}^2$.

In addition, Videnovic *et al* [20] propose that the argon effect is due to the efficient production of H_3^+ via the production of H_2^+ by the reaction



The contribution produced by this pathway is also very unlikely to be significant due to the short lifetime of the excited state and corresponding negligible population.

Since hydrogen usually has a low degree of ionization, 10^{-4} , and the cross section for electron ionization of molecular hydrogen:



is 10^{-16} cm^2 , this reaction is expected to be the major source of H_2^+ even in argon–hydrogen plasmas [27]. The participation of argon should be insignificant when species concentrations, lifetimes, and reaction cross sections are considered. Furthermore, Videnovic *et al* ignored other processes which could diminish the acceleration of hydrogen ions in

the cathode fall region. For example, the dissociative recombination cross section for H_3^+ given by



is 10^{-14} cm^2 [27], about an order of magnitude greater than the cross section of equation (13) or (16). Thus, 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* [20] propose that the absence of line broadening with argon alone is explained by a large cross section for charge exchange which prevents the acceleration of argon ions to high energies. For example, the charge-exchange reaction



(*s* stands for slow, and *f* stands for 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* [20] 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* [20].

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 ($T_g(\text{Ar}/\text{H}_2) = T_g(\text{H}_2) = 1000 \text{ K}$, $P(\text{Ar}/\text{H}_2) = 320 \text{ Pa}$, and $P(\text{H}_2) = 228 \text{ Pa}$). However, they assumed a cathode fall region that was twice the length of that in the hydrogen case ($L = 0.158$ versus 0.085 cm), and even if this factor-of-two difference existed, it could be 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 $P(\text{H}_2) = 150 \text{ Pa}$ [31], whereas it is in the case with $P(\text{Ar}/\text{H}_2) = 320 \text{ Pa}$.

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, greater (125 eV) than that observed in the case of an argon–hydrogen mixture (95 eV) [31].

A further internal inconsistency arises from the explanation of the argon effect by Radovanov *et al* [32] compared to that of Videnovic *et al* [20]. Radovanov *et al* [32] 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 travelling 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* [20] that allow ions to accelerate and fast H to propagate; yet it must be highly collisional according to Radovanov *et al* [32], in order to form the excited $n = 3$ atoms. This explanation is even less plausible given our observation with microwave plasmas that the largest broadening was observed with helium–hydrogen followed by argon–hydrogen, but no broadening was observed with neon or xenon with hydrogen [13].

Videnovic *et al* [20] encounter another problem with the observation that the H temperature in the negative glow is higher than that in the cathode fall region. Their explanation is that fast

neutrals are additionally excited by collisions with electrons. Yet, the electron temperature T_e in these plasmas is only about 1 eV [31], whereas the H-atom temperature T_H in the negative glow region was about 50 eV. Since $T_H \gg T_e$ the energetic atoms would be expected to heat the electrons rather than the reverse, as proposed by Videnovic *et al* [20].

Prior studies that reported high H temperatures attributed the observation to acceleration of ions in high electric fields at the cathode fall region [20, 23, 31, 32] and an external field Stark effect [20]. We believe this is the first report of similar observations with a microwave plasma having no high field present. The microwave field couples to electrons, not ions. And the high H temperature cannot be attributed to the mechanisms proposed previously. In fact, in the microwave case, the argon atoms and ions would have the highest energies since they have the largest cross section for electron collisions.

No hydrogen species, H^+ , H_2^+ , H_3^+ , H^- , H, or H_2 , responds to the microwave field; rather, only the electrons respond. But the measured electron temperature was about 1 eV, whereas the measured H temperature was 110–130 eV. This requires that $T_H \gg T_e$. This result cannot be explained by electric field acceleration of charged species. In microwave-driven plasmas, there is no high electric field in a cathode fall region ($>1 \text{ kV cm}^{-1}$) to accelerate positive ions as proposed previously [20, 23, 31, 32] to explain significant broadening in hydrogen-containing plasmas driven by high-voltage electrodes. It is impossible for H or any H-containing ion which may give rise to H to have a higher temperature than the electrons in a microwave plasma. The observation of excessive Balmer line broadening in a microwave-driven plasma requires a source of free energy.

A source of energy other than that provided by the electric field or known chemical reactions must be considered. Excessive line broadening was only observed in the cases where Ar^+ was present, which could provide a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen, whereas plasmas with chemically similar xenon control that do not provide gaseous atoms or ions that have electron ionization energies which are a multiple of 27.2 eV showed no effect with the addition of 10% hydrogen. These results support the rt-plasma mechanism. Thus, an argon microwave discharge with hydrogen may have formed an rt-plasma that gave rise to the observed elevated hydrogen temperature, electron temperature, and neutral gas temperature.

The argon-ion catalyst provides a net positive enthalpy of reaction of 27.2 eV (i.e. it resonantly accepts the nonradiative energy transfer from hydrogen atoms and releases the energy to the surroundings which heat up). The thermalization of the 27.2 eV is consistent with the observation by Djurovic and Roberts [23] and Radovanov *et al* [32] of no directional effects of the Doppler broadening due to the applied electric field and the average energy of 23.8 and 28 eV, respectively, of the fast H excited atoms that was similar throughout the whole interelectrode region of the discharge over a wide range of gas pressures, applied rf voltages, and hydrogen concentration in Ar– H_2 mixtures. In addition, at low pressures, Radovanov *et al* [32] observed Ar^+ and ArH^+ kinetic energy distribution profiles with an edge at about 27.2 eV.

rt-plasmas formed with hydrogen–potassium mixtures have been reported previously [6, 14] wherein the plasma decayed with a two-second half-life when the electric field was set to zero. This was the thermal decay time of the filament which dissociated molecular hydrogen to atomic hydrogen. This experiment showed that hydrogen line emission was occurring even though the voltage between the heater wires was set to and measured to be zero, and it indicated that the emission was due to a reaction of potassium atoms with atomic hydrogen. Potassium atoms ionize at an integer multiple of the potential energy of atomic hydrogen, $m \times 27.2 \text{ eV}$. The enthalpy of

ionization of $\text{K}-\text{K}^{3+}$ has a net enthalpy of reaction of 81.7426 eV, which is equivalent to $m = 3$. K^{3+} and the formation of the corresponding hydride were detected by EUV spectroscopy of an rt-plasma [9].

4. Conclusions

Upon the addition of 5% argon to a hydrogen plasma, the Lyman alpha emission was observed to increase by about an order of magnitude which suggested that one or more of the plasma temperatures may be elevated, whereas no effect was observed with xenon. Line broadening of the hydrogen Balmer lines provides a sensitive measure of the number and energy of excited hydrogen atoms in a plasma. The widths of the 656.3 nm Balmer α lines emitted from microwave discharge plasmas having atomized hydrogen from pure hydrogen alone and a mixture of 10% hydrogen and argon or xenon were measured with a high-resolution (± 0.006 nm) visible spectrometer. The energetic hydrogen-atom density and energies were determined from the broadening, and it was found that argon–hydrogen showed significant broadening corresponding to an average hydrogen-atom temperature of 110–130 eV, whereas pure hydrogen and xenon–hydrogen showed no excessive broadening corresponding to an average hydrogen-atom temperature of ≈ 3 eV. Similarly, the average electron temperature T_e for the argon–hydrogen was high, $11\,600 \pm 5\%$ K, compared to 4800 ± 5 , 4980 ± 5 , and $6500 \pm 5\%$ K for argon alone, xenon alone, and xenon–hydrogen plasmas, respectively.

The gas temperature provides a means to estimate the power output of the cell. With a microwave input power of 40 W, the gas temperature of an argon plasma increased from 400 to over 750 °C with the addition of 3% flowing hydrogen, whereas the 400 °C temperature of a xenon plasma under identical conditions was essentially unchanged with the addition of hydrogen. The thermal output power was estimated to be 76 W. Since the hydrogen flow rate was 1 sccm, an estimate of the corresponding energy balance was over -1×10^4 kJ (mol H_2)⁻¹ compared to the enthalpy of combustion of hydrogen of -241.8 kJ (mol H_2)⁻¹.

The observed excessive line broadening corresponding to an elevated hydrogen-atom temperature, an elevated T_e , and an elevated plasma gas temperature were only observed in the case where Ar^+ , an ion which provides a net enthalpy of reaction of a multiple of the potential energy of the hydrogen atom, and present with atomic hydrogen. Nonequilibrium plasma conditions may explain the elevation of one these temperatures over another [33]; however, the elevation of all three temperatures indicates power dissipation in the plasma in addition to the microwave input. The source of additional power corresponding to the elevated temperatures may be an energetic reaction of atomic hydrogen caused by a resonance energy transfer between hydrogen atoms and Ar^+ .

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