INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 33 (2008) 2419–2432

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Evidence of energetic reactions between hydrogen and oxygen species in RF generated H_2O plasmas

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ARTICLE INFO

Article history:
Received 11 December 2007
Received in revised form
29 February 2008
Accepted 29 February 2008
Available online 22 April 2008

Keywords:
Plasma
RF
Balmer series
Line broadening
Water

ABSTRACT

Selective H-atom line broadening was found to be present throughout the volume (14 cm ID × 38 cm length) of low pressure (0.03–0.4 Torr) H_2O only RF plasmas generated in an RF capacitively coupled parallel-plate cell. An exhaustive study of the first four Balmer lines in water plasmas operated over a range of pressures and absorbed powers revealed significant trends. Of greatest interest was the finding that at low pressures (ca. <0.08 Torr) a significant fraction (between 10% and 40%) of the atomic hydrogen was 'hot' with energies greater than 40 eV. The magnitude of the line broadening was found not only to be pressure dependent, but also to be a weak function of the energy absorbed by the system. The degree of broadening was virtually independent of the position studied within the RF capacitively coupled parallel-plate cell, similar to the finding for H_2/He and H_2/Ar plasmas in the same capacitively coupled cell, reported elsewhere. In contrast to the atomic hydrogen lines, no broadening was observed in oxygen species lines at low pressures. Also, in 'control' H_2/Xe plasmas run in the same cell at similar pressures and adsorbed power, little broadening of either atomic hydrogen, Xe or any other lines was observed. The values of the line broadenings observed in the low pressure water plasmas, and the fact that they were observed throughout the volume, are consistent with predictions of the Mills model, CQM, of populating fractional quantum states in H-atoms via catalytic resonant transfer processes. In particular CQM predicts that O_2 can act as a catalyst for the RT process, and spectroscopy shows the water plasma contain a significant O_2 population. Standard physics models of preferential hydrogen line broadening, developed explicitly for hydrogen/argon mixtures, are clearly not consistent with any aspect of the behavior observed in the water plasma data reported here.

1. Introduction

Numerous studies show that the Balmer lines of atomic hydrogen are significantly broadened in high field regions of RF plasmas in RF capacitively coupled parallel-plate cell type cells. Most of these reports regard broadening in H_2/Ar plasmas [1–14], although there are also reports of Balmer series line broadening in helium-hydrogen plasmas generated in capacitively coupled cells [15], water vapor plasmas in microwave plasmas [16], as well as broadening in the presence of a number of catalysts, such as strontium in GEC type cells, filament cells and even DC discharges [17–24].

There is considerable controversy regarding the origin of this effect. On one side are scientists who believe they represent the main stream of physics thought. This group has developed a set of related models that are all based on the

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doi:10.1016/j.ijhydene.2008.02.079

same principle premise: All the line broadening results from field acceleration of ionic species. Thus these models as a group are called field effect (FA) models. The most recent subset of these may be called for convenience collisional field effect models (FA-C), and the authors indicate these models supercede the earlier versions [12–14]. To be more specific, all the models contain these elements: (i) For a time hydrogen exists as an ionic species (e.g. H_2^+) in a high field region. During this time it gains energy from the field. (ii) At some point, the ionic form gains an electron, a process facilitated by argon, but not requiring argon. (iii) At some point the molecular species, dissociates [2,3]. Finally, (iv) those high velocity atomic species that are in an excited state emit photons, generating the usual Balmer series. The FA-C models include an additional postulate: High energy species, generally atoms, 'bounce' off electrodes, then collide with hydrogen species to generate high energy hydrogen. This accounts for the symmetry of the line broadening, that is both red and blue shifts are observed on the broadened lines. All these models require a high field locally (excited states have very short lifetimes) and all imply that the Doppler broadening should be greatest when observed along the direction of field.

Tests designed to disprove the FA models, can be designed. After all, it is easier to disprove a model than it is to prove one. In particular, we have designed, and conducted [1], experiments to test the following predictions. (i) Line broadening, according to the FA models will be most pronounced in plasmas containing argon. Argon is 'called out' as a necessary ingredient because of the large x-section for charge exchange with hydrogen [3,4,6]. Moreover, all papers supporting the FA model are done with pure hydrogen or with mixed Ar–H_2 plasmas. (ii) Line broadening will not be observed at all in low field regions, hence the exclusive observational focus on broadening in the cathode fall region in all of the FA model papers [1–14,25]. Finally, (iii) all FA models should predict impact of the angle of observation relative to field direction on the observed extent of Balmer broadening [14,25].

Our tests, including the present one, produced results inconsistent with the predictions of the FA models. For example, the plausibility of FA models was greatly eroded by a recently published paper by our group on an exhaustive study of RF generated H_2/Ar plasmas in the same RF capacitively coupled parallel-plate cell apparatus [1]. Several features of the line broadening observed in that study are clearly not consistent with FA models. Specifically, it was demonstrated that: (i) the observed Doppler broadening is virtually independent of field direction, (ii) line broadening was found throughout the cell, including in areas of virtually no field, (iii) the impact of field strength on the measured broadening was found to be minimal, (iv) the intensity of the broadened Balmer lines was in some cases highest away from the high field region and (v) hot atomic hydrogen translation energy was nearly two orders of magnitude hotter than both the excitation temperature and the electrons in the system. In another study it was found that extreme line broadening is found in the Balmer series of water plasmas generated with microwave power [16] and selective line broadening observed away from the coupler. It is generally understood that in low pressure plasmas (ca. <1 atmosphere) little energy is picked up by the ions, even in the sheath. Moreover, in the system in which line broadening was observed, the sheath thickness (roughly equal the Debye length of the ambipolar ion–electron pair) is much smaller than the tube radius, hence generally neglected in bulk plasma models [26].

Some supporters of the FA family of models have clearly, but inadvertently, produced data that are inconsistent with the FA models. For example, in studies designed to show that line broadening of Balmer lines in Ar/H_2 plasmas is greatest when observed along the direction of field, showed no effect. Line broadening was found to be independent of the direction of observation [14,25].

As noted earlier, there is an alternative to the FA models. This model, is based on a new theory of quantum mechanics, the classical quantum mechanics (CQM) model. This model is not acceptable to many in the physics community because it requires that hydrogen exists in states heretofore regarded as impossible. Still, although controversial, the new model does apparently predict the observed features of line broadening observed in RF and microwave plasmas. It is argued here and elsewhere, that the broadening is consistent with a 'chemical' reaction, predicted by CQM, between helium and hydrogen atoms, or helium and argon, or oxygen atoms and hydrogen atoms throughout the volume of the cell. It must be noted that the word 'consistent' was carefully selected. It is intended to be an accurate description of the relationship between data and theory, as regards Balmer line broadening, and possibly other types of experimental studies, without implying an endorsement of the theory. The term 'consistent' is not the same as 'proven' or 'demonstrated'. A theory that is 'consistent' with existing data is one that is not *disproven*, and such a theory must still be considered 'reasonable' and an appropriate subject for additional study/testing.

In the earlier reports [1,5,15,24], including an earlier version of the present paper [27], it was noted that the magnitude of the broadening was completely consistent with the CQM model for such a reaction process. Another finding in that study, also consistent with the CQM model, was that in H_2/Xe plasmas there was no broadening of either hydrogen or Xe lines outside of the electrode region.

In the CQM model energy is evolved when electrons drop into fractional quantum states [28,29]. The process is catalytic rather than spontaneous. Thus, the process does not require a 'field', but only an environment in which H atoms and catalytic species can collide/interact. In order for a species to function as a resonant transfer (RT) catalyst it must have an energy separation between electron states of some multiple of one Hartree. For He and Ar^+ (subjects of earlier related papers [1,15]) there are allowed transitions which release 27.2 eV. In other words, according to CQM, the drop of energy of an electron in hydrogen in its 'ground state' to the lower energy ('hydrino') requires a catalytic species. The catalytic species must have an excited energy transition (e.g. ground to excited state) that is capable of temporarily adsorbing the energy released by a hydrogen electron falling to a lower energy state. In particular, there are allowed RT catalytic processes between H atoms and He and Ar^+ that can temporarily adsorb the energy released as a 'ground state' hydrogen electrons drops from the $n=1$ to the $n=\frac{1}{2}$ state, releasing 27.2 eV in the process. Thus, in both H_2/He and H_2/Ar plasmas it is expected that line broadening due to RT processes will equal around 27 eV. This model is thus consistent with the observations made in the preceding work including the finding that Doppler broadening of H-atom Balmer lines is found throughout the entire volume of a H_2/He plasma created in a GEC cell, and not merely in the vicinity of the electrodes.

The present work was intended to further test the CQM model. It was designed to test for consistency of the theory in an environment never previously tested, that is one containing O_2 'catalysts' and H atoms. As the CQM theory predicts Balmer line broadening of a larger magnitude in this mixture than in Ar/H_2 plasmas, then the absence of Balmer series line broadening greater than that observed in a Ar/H_2 plasmas would be a possible component of a 'dis-proof' of the CQM theory. Indeed, in an H_2O plasma O_2 is present, and there are two body collisions that can contribute a maximum of either 54.4 or 108.8 eV to atomic translation according to CQM (more later). This is larger than the energy release expected from an Ar^+ catalyst and the latter is larger than that expected from a He^+ catalyst according to the CQM theory (see above). Thus, at a minimum, for the present experiments to 'fail to disprove' CQM, there must be line broadening in a water plasma, and the magnitude of this broadening must be greater than that observed in H_2/He and H_2/Ar plasmas.

The experimental results are consistent with the CQM model: measured Balmer series line broadening throughout the cell (up to 15 cm from the electrodes) for low pressure plasmas ($<$0.08 Torr) with values generally greater than that observed in either H_2/Ar or / H_2/He plasmas, independent of position within the plasma, and weakly dependent on the absorbed power. Thus, it can be argued that the results of this study have not disproved the CQM model. To re-iterate: The sole conclusion reached herein as regards CQM is that we have failed to disprove the model.

The implications of the results in terms of the 'consistency' of the CQM model with Balmer line broadening can be ignored, and still this study remains very valuable. Indeed, it contains the first direct mapping of the broadening of Balmer series lines for water plasmas in an RF capacitively coupled parallel-plate apparatus. Moreover, it is the first detailed study of the impact of applied power and operating pressure. In other respects the current results reinforce earlier studies of similar phenomenon reported elsewhere. For example, there are earlier reports of selective Balmer series line broadening (ca. 55 eV) and H-atom excitation temperature inversion (similar magnitude) of water plasmas generated in microwave discharge cavities [16]. Other work consistent with the present findings include the EUV spectra of H_2/He lines which show nearly all the lines predicted by the theory [30–32], and detailed water bath calorimetric studies of RT and non-RT plasmas created with Evenson microwave couplers that show significant 'excess' energy production by the RT plasmas [33].

2. Experimental

2.1. Plasma hardware

All plasmas were generated in a RF capacitively coupled parallel-plate cell apparatus [5,11,34] held at 0.5 Torr. This system, shown in Fig. 1 (a modification of one shown elsewhere [1]), consists of a large cylindrical (14 cm ID× 36 cm length) pyrex chamber containing two parallel steel circular (8.25 cm diameter) plates, placed about 1 cm apart at the center. RF power from a RF VII, Model RF 5 13.6 MHz power supply was sent to the plates through 8 mm diameter steel feeds, which entered the chamber through standard ultratorr fittings, one on each end of the chamber. Gases, UHP grade (99.999%) H_2 and Xe, were metered into the chamber through ultratorr fittings at one end, about 18 cm from the electrodes, using two mass flow controllers (MKS). The entire RF system, but not the pump nor the spectrometer, was housed inside a Faraday cage. Small openings were made to allow power, light fiber, gas, pump lines, etc. to enter.

Water vapor was generated by pumping on a reservoir (about 20 cc) of distilled, de-ionized water. The flow rate was not directly controlled, but rather a needle valve was adjusted to maintain the desired pressure, as measured by a MKS baratron placed above the Welch two stage rotary vane oil sealed vacuum pump (Model 8920) with a rated capacity of 218 l min^{-1}. This pump was attached to the chamber with a 1 cm ID ultratorr fitting at the end opposite that at which gas entered. The entire system, except the spectrometer was encased in a copper screen Faraday cage.

2.2. Spectrometer

The spectrometer system used in this study, described in detail elsewhere [35], is built around a 1.25 m visible light instrument from Jvon-Spex with a holographic ruled diffraction grating (1800 g mm^{-1}), with a nearly flat response between 300 and 900 nm, and the slit was set at 10 μm in all cases. Light was collected using a light fiber bundle consisting of 19 200 μm fibers and a CCD for a detector. Light was input to the spectrometer from the light fiber, placed either near an end of the chamber, approximated 15 cm from either electrode, or in a quartz insert tube 1 cm in diameter, that ended about 1 cm from the edge of the electrodes. The fiber placed directly above the electrodes oriented was 'tilted' ~15° relative to vertical of the chamber in all cases.

It is important to note that tests with a red laser with the system open clearly showed that light emanating from the region between the plates could not have reached the 'hooded' fiber optic probe when it was positioned at either end. Indeed, our tests showed that light no closer than 15 cm from the plate region reached the fiber optic probe. These readings are consistent with the listed 9° acceptance angle given with the probe. That angle indicates that a 1 cm diameter 'spot' would be encompassed by the acceptance cone even at the far side of the plasma cylinder from the probe, that is, 15 cm from either collection points 1 or 3. Moreover, the probes were oriented such that the acceptance cone should 'miss' the power feeds by several centimeters.

In most cases in which data were used for computations (e.g. excitation temperatures), it was collected for the same time over the same wavelength region. Balmer series spectral lines were fit using three Gaussians, one for the 'cold' ($<$0.15 eV) hydrogen, one for 'warm' hydrogen ($<$2 eV) and the third for 'hot' ($>$10 eV) hydrogen. It is notable that the fittings achieved were excellent, producing $R^2>0.98$ in all cases. In all cases, initial fits were made with two Gaussians.

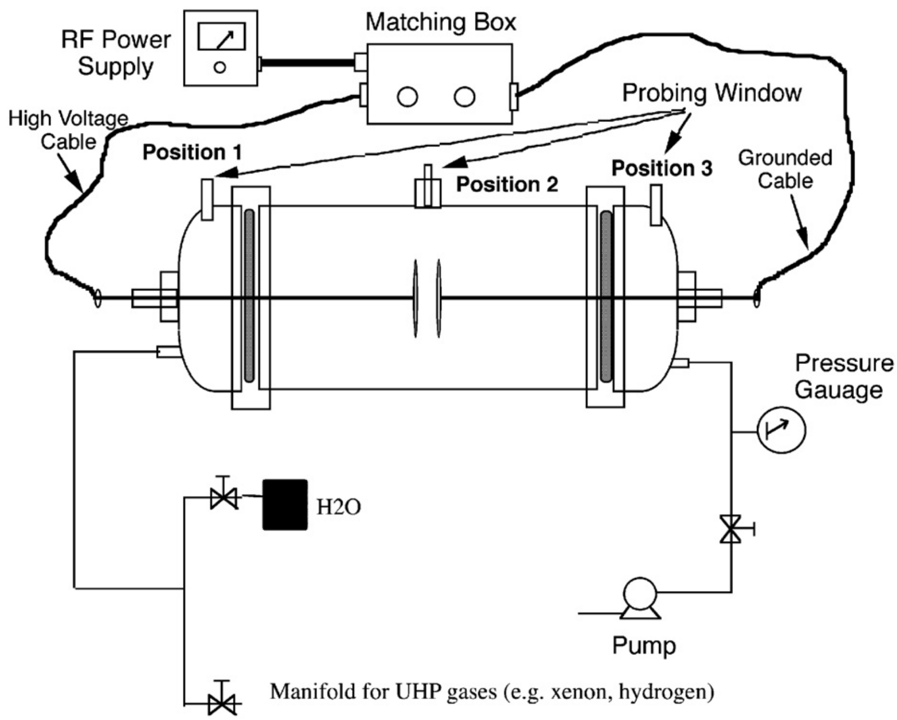

Fig. 1 – Cylindrical RF Plasma System. Length: 35 cm, radius 14 cm. Positions 1 and 3 are 15 cm from the center. Note, most data collected at Position 2 (high field) and at Position 3 ('grounded electrode' and gas exit position).

This was done to establish that the fitting routine did not introduce any unsupportable result. That is, in all cases the visual observation of one clearly 'narrow' component and one very broad component were qualitatively matched, (and to the eye, well matched) by two fitted Gaussian peaks. The 'warm' peak was then added to obtain an excellent R^2 value. One reason for the excellent fits was the absence of any signal in the relevant spectral area of the Balmer α and β lines of the water plasma (Fig. 2a). In contrast, there is 'signal' in the same regions for the H_2/Xe plasma (Fig. 2c).

3. Results

A significant amount of data were collected in order to reliably detect trends in the H-atom line broadening in water plasmas as a function of plasma operating conditions. Data on line broadening was systematically collected for the Balmer α, β, γ and δ lines at two positions, between the plates (Position 2) and at the end of the GEC cell closest to the pump (Position 3), and the ground electrode which is about 15 cm from the electrodes. No data are reported from the region near the gas input/powered electrode end because the hydrogen signal was so weak that we judged the fitted values to be unreliable. In Tables 1–6, measured values of H-atom α and β line broadening for water plasmas at both positions, at 10 or more pressures, at three absorbed power levels (100, 150 and 200 W), are presented. The data for the γ and δ lines is not presented as it is considered less reliable as the intensity of these lines is significantly lower. Also, the trends in Doppler energy of the hot hydrogen as a function of pressure, and applied power is virtually identical to those observed from the α and β lines, thus the data for the higher energy transitions in the Balmer series is regarded as somewhat redundant, and hence not essential to the arguments presented.

In Fig. 2 typical peaks are shown as well as the fit of the data to three peaks. All of the data can be well fitted to three peaks. This supports the supposition that the 'hot' part of the lines must be Doppler broadening. All other mechanisms would not produce a three component line, but only a single component line.

Data on the impact of pressure for any given adsorbed power is plotted (Figs. 3 and 4) to show that the energy of the hot hydrogen (as well as cold and warm atomic hydrogen) is independent of position. These same plots show that there is a strong dependence of pressure on the Doppler energy of the hot hydrogen. A comparison between the plots also suggests a dependence on the absorbed energy. In sum, the results reported here clearly show that throughout GEC cell plasmas generated at low pressures (ca. <0.08 Torr) from pure water, there is 'hot' atomic hydrogen, of an apparent energy between 40 and 55 eV from the H_α line (approx. 450,000 to 550,000 K) and nearly 70 eV from the H_β line.

No other species in these plasmas, specifically molecular hydrogen and various oxygen species, were found to be 'hot' or even 'warm' at these low pressures. The magnitude of the H-atom Doppler broadening was found to be weakly dependent on the amount of energy adsorbed by the plasma, and strongly dependent on the operating pressure, dropping sharply above approximately 0.1 Torr in all cases. Yet, under all operating conditions the magnitude of the broadening at 15 cm from the electrodes was very close to the magnitude within the region between the plates.

Table 1 – Analysis of H_α lines in 100 W (RF power) water plasmas

Position/Balmer lines	Pressure (Torr)	Doppler energy cold H (eV)	Doppler energy warm H (eV)	Doppler energy hot H (eV)	Area ratio hot/all
2/H_α	0.23	0.122	1.336	11.6	0.250
2/H_α	0.19	0.123	1.373	10.8	0.269
2/H_α	0.17	0.122	1.412	11.0	0.288
2/H_α	0.15	0.123	1.470	11.8	0.287
2/H_α	0.13	0.124	1.502	12.6	0.291
2/H_α	0.12	0.122	1.459	12.5	0.303
2/H_α	0.10	0.121	1.475	14.1	0.287
2/H_α	0.09	0.121	1.517	16.2	0.263
2/H_α	0.08	0.119	1.560	23.1	0.245
2/H_α	0.07	0.118	1.517	35.0	0.245
2/H_α	0.06	0.117	1.291	37.9	0.252
2/H_α	0.05	0.116	1.193	39.2	0.251
2/H_α	0.04	0.114	1.195	42.1	0.218
2/H_α	0.03	0.114	1.360	42.4	0.159
2/H_α	0.02	0.104	1.539	37.3	0.078
3/H_α	0.18	0.124	1.043	8.2	0.135
3/H_α	0.17	0.118	1.124	12.4	0.137
3/H_α	0.15	0.122	1.136	15.1	0.127
3/H_α	0.13	0.117	1.176	23.2	0.133
3/H_α	0.11	0.120	1.244	20.7	0.126
3/H_α	0.09	0.118	1.218	19.1	0.141
3/H_α	0.08	0.118	1.261	34.4	0.136
3/H_α	0.07	0.116	1.263	23.3	0.135
3/H_α	0.06	0.118	1.371	29.7	0.156
3/H_α	0.05	0.115	1.350	37.1	0.211
3/H_α	0.04	0.115	1.252	37.6	0.250
3/H_α	0.03	0.113	1.432	32.2	0.083

Table 2 – Analysis of H_α lines in 150 W (RF power) water plasmas

Position/Balmer lines	Pressure (Torr)	Doppler energy cold H (eV)	Doppler energy warm H (eV)	Doppler energy hot H (eV)	Area ratio hot/all
2/H_α	0.20	0.126	1.497	12.7	0.258
2/H_α	0.17	0.121	1.446	12.6	0.294
2/H_α	0.15	0.123	1.536	14.0	0.300
2/H_α	0.13	0.123	1.600	15.9	0.294
2/H_α	0.11	0.119	1.478	17.1	0.304
2/H_α	0.09	0.118	1.562	27.1	0.281
2/H_α	0.08	0.119	1.594	43.7	0.303
2/H_α	0.07	0.117	1.404	44.1	0.358
2/H_α	0.06	0.117	1.110	48.9	0.345
2/H_α	0.04	0.117	1.163	49.0	0.278
2/H_α	0.03	0.113	1.323	52.1	0.203
2/H_α	0.02	0.111	1.687	50.7	0.145
3/H_α	0.20	0.119	1.161	19.1	0.159
3/H_α	0.18	0.124	1.250	25.5	0.148
3/H_α	0.15	0.126	1.167	20.9	0.160
3/H_α	0.13	0.119	1.262	24.4	0.165
3/H_α	0.11	0.118	1.325	23.5	0.145
3/H_α	0.09	0.115	1.410	43.7	0.189
3/H_α	0.08	0.116	1.554	41.5	0.277
3/H_α	0.07	0.117	1.404	44.4	0.359
3/H_α	0.05	0.115	1.378	45.2	0.335
3/H_α	0.04	0.117	1.376	43.6	0.260

Table 3 – Analysis of H_α lines in 200 W (RF power) water plasmas

Position/Balmer lines	Pressure (Torr)	Doppler energy cold H (eV)	Doppler energy warm H (eV)	Doppler energy hot H (eV)	Area ratio hot/all
2/H_α	0.22	0.123	1.369	11.6	0.268
2/H_α	0.18	0.125	1.459	12.4	0.296
2/H_α	0.15	0.122	1.520	14.3	0.313
2/H_α	0.13	0.122	1.618	17.5	0.310
2/H_α	0.12	0.121	1.668	23.7	0.306
2/H_α	0.11	0.119	1.605	36.3	0.307
2/H_α	0.09	0.115	1.295	51.6	0.414
2/H_α	0.07	0.117	1.174	52.1	0.432
2/H_α	0.05	0.116	1.142	52.0	0.350
2/H_α	0.04	0.116	1.252	53.3	0.260
2/H_α	0.03	0.110	1.585	53.2	0.159
3/H_α	0.21	0.119	1.108	13.9	0.171
3/H_α	0.17	0.121	1.149	14.3	0.172
3/H_α	0.13	0.123	1.158	15.0	0.181
3/H_α	0.11	0.124	1.225	20.7	0.188
3/H_α	0.09	0.119	1.252	23.2	0.204
3/H_α	0.08	0.120	1.370	31.2	0.203
3/H_α	0.08	0.117	1.490	44.8	0.256
3/H_α	0.07	0.116	1.421	50.4	0.412
3/H_α	0.05	0.116	1.352	50.6	0.421
3/H_α	0.04	0.115	1.432	47.4	0.244
3/H_α	0.03	0.122	2.045	x	0.000

Table 4 – Analysis of H_β lines in 100 W (RF power) water plasmas

Position/Balmer lines	Pressure (Torr)	Doppler energy cold H (eV)	Doppler energy warm H (eV)	Doppler energy hot H (eV)	Area ratio hot/all
2/H_β	0.21	0.143	1.644	11.0	0.203
2/H_β	0.17	0.156	1.936	25.7	0.172
2/H_β	0.16	0.239	2.480	14.7	0.175
2/H_β	0.14	0.132	1.820	19.7	0.216
2/H_β	0.12	0.142	1.944	18.4	0.198
2/H_β	0.11	0.175	3.331	17.0	0.148
2/H_β	0.10	0.134	1.841	13.9	0.219
2/H_β	0.08	0.127	1.699	22.6	0.193
2/H_β	0.07	0.127	1.730	28.6	0.207
2/H_β	0.06	0.128	1.679	38.8	0.219
2/H_β	0.05	0.129	1.679	39.5	0.176
2/H_β	0.04	0.128	1.648	46.8	0.148
2/H_β	0.03	0.110	1.698	22.4	0.070
3/H_β	0.20	0.138	1.191	5.7	0.142
3/H_β	0.16	0.145	1.421	8.2	0.104
3/H_β	0.14	0.137	1.324	5.3	0.030
3/H_β	0.12	0.138	1.454	26.6	0.107
3/H_β	0.10	0.132	1.367	12.0	0.099
3/H_β	0.09	0.127	1.396	6.9	0.099
3/H_β	0.08	0.123	1.446	14.2	0.124
3/H_β	0.07	0.126	1.505	11.5	0.111
3/H_β	0.06	0.120	1.810	52.3	0.251
3/H_β	0.05	0.122	1.890	58.9	0.176
3/H_β	0.03	0.122	1.728	63.4	0.092

It is notable that the fraction of H-atoms that are hot is somewhat impacted by position within the cell. As shown in Fig. 5, the fraction of 'hot' hydrogen is strongly dependent on pressure, and somewhat on adsorbed power, and is generally slightly higher between the plates than it is at the end of the cell, 15 cm from the electrodes.

Table 5 – Analysis of H_β lines in 150 W (Rf power) water plasmas

Position/Balmer lines	Pressure (Torr)	Doppler energy cold H (eV)	Doppler energy warm H (eV)	Doppler energy hot H (eV)	Area ratio hot/all
$2/H_\beta$	0.23	0.139	1.840	21.9	0.197
$2/H_\beta$	0.17	0.122	1.711	11.9	0.268
$2/H_\beta$	0.15	0.130	2.033	26.0	0.224
$2/H_\beta$	0.13	0.123	2.011	28.7	0.193
$2/H_\beta$	0.11	0.131	2.020	34.5	0.241
$2/H_\beta$	0.10	0.129	1.887	36.9	0.273
$2/H_\beta$	0.08	0.127	1.643	43.2	0.331
$2/H_\beta$	0.07	0.126	1.580	50.6	0.338
$2/H_\beta$	0.06	0.127	1.643	54.5	0.258
$2/H_\beta$	0.06	0.126	1.579	41.9	0.199
$2/H_\beta$	0.05	0.110	1.780	31.4	0.084
$3/H_\beta$	0.22	0.136	1.359	21.0	0.115
$3/H_\beta$	0.18	0.116	1.325	13.6	0.123
$3/H_\beta$	0.15	0.140	1.515	18.6	0.069
$3/H_\beta$	0.13	0.129	1.639	27.9	0.063
$3/H_\beta$	0.11	0.131	1.647	33.2	0.106
$3/H_\beta$	0.09	0.121	1.747	27.1	0.120
$3/H_\beta$	0.08	0.113	1.898	39.8	0.181
$3/H_\beta$	0.07	0.118	1.881	43.3	0.284
$3/H_\beta$	0.05	0.120	1.746	53.0	0.338
$3/H_\beta$	0.04	0.120	1.850	49.9	0.304
$3/H_\beta$	0.03	0.122	1.836	45.6	0.119

Table 6 – Analysis of H_β lines in 200 W (Rf power) water plasmas

Position/Balmer lines	Pressure (Torr)	Doppler energy cold H (eV)	Doppler energy warm H (eV)	Doppler energy hot H (eV)	Area ratio hot/all
$2/H_\beta$	0.22	0.131	1.734	13.6	0.228
$2/H_\beta$	0.18	0.127	1.920	21.1	0.223
$2/H_\beta$	0.16	0.129	1.930	23.9	0.247
$2/H_\beta$	0.14	0.125	2.046	33.4	0.246
$2/H_\beta$	0.12	0.100	1.901	35.2	0.257
$2/H_\beta$	0.10	0.123	1.913	29.7	0.219
$2/H_\beta$	0.08	0.126	1.870	42.2	0.311
$2/H_\beta$	0.07	0.129	1.837	52.7	0.341
$2/H_\beta$	0.05	0.139	1.471	46.7	0.380
$2/H_\beta$	0.04	0.125	1.594	58.9	0.308
$2/H_\beta$	0.03	0.113	1.740	54.5	0.164
$3/H_\beta$	0.15	0.124	1.550	25.1	0.152
$3/H_\beta$	0.13	0.120	1.719	39.8	0.174
$3/H_\beta$	0.11	0.122	1.812	52.0	0.208
$3/H_\beta$	0.09	0.122	1.917	62.7	0.383
$3/H_\beta$	0.07	0.121	1.750	61.4	0.479
$3/H_\beta$	0.05	0.120	1.793	54.5	0.425
$3/H_\beta$	0.04	0.122	1.877	56.3	0.400
$3/H_\beta$	0.03	0.119	1.700	42.0	0.251
$3/H_\beta$	0.02	0.127	1.549	15.3	0.156

Simple comparisons can be made between the results of this study of H_2O plasmas and earlier studies, performed in the same GEC cell, of H_2/He plasmas. First, it is notable that there is no overlap in the Doppler energies of the hot hydrogen measured for the two different plasmas, despite the fact that the physical arrangement of the cell (e.g. electrode separation) was virtually identical in both cases. For the water plasma the average broadening is always at least 10 eV greater than that found in the H_2/He plasma. Also, one feature similar to that found with the H_2/He plasma, is

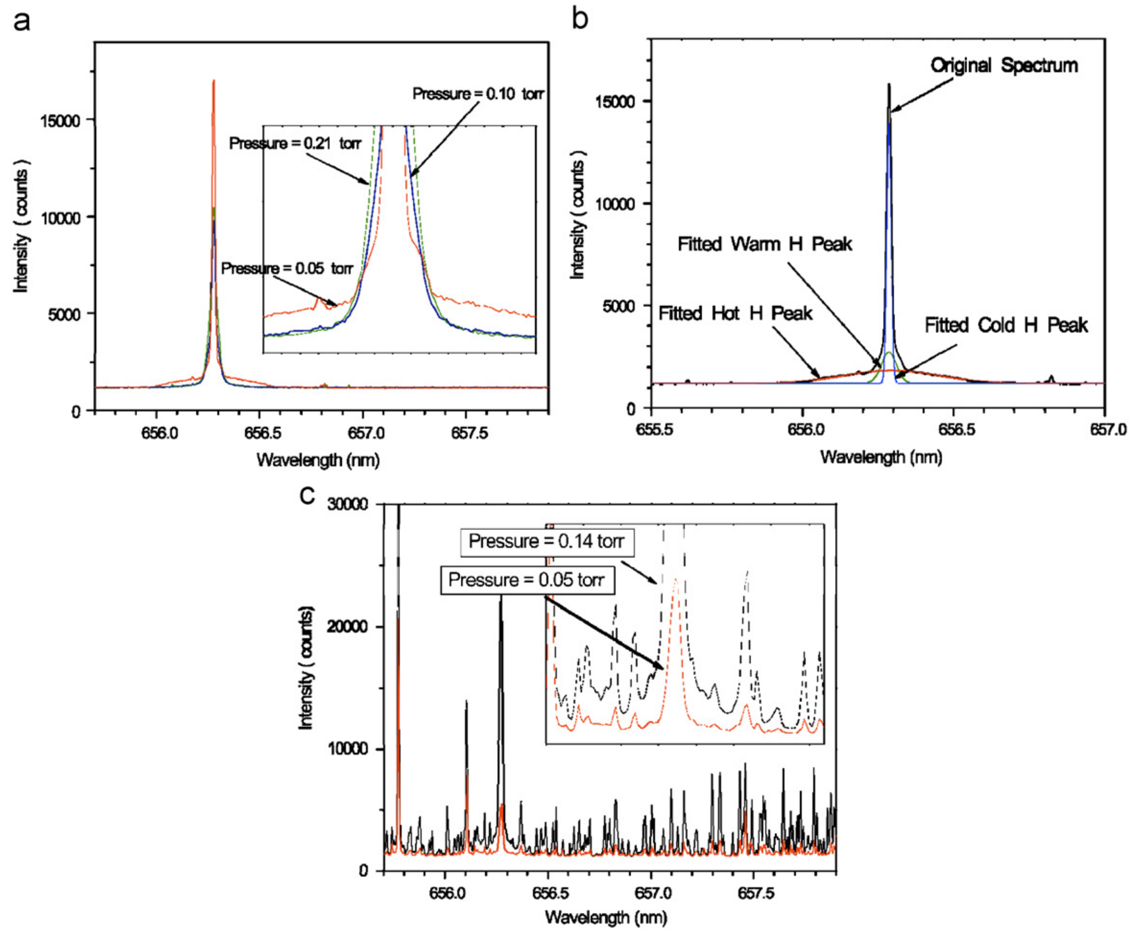

Fig. 2 – Hydrogen Balmer α lines indicate presence of hydrogen atoms with energy in excess of 40 eV. (a) At 0.05 Torr, 150 W, Position 3, Doppler broadening from H atoms with energies greater than 40 eV is seen at the base of the H_α peak. No 'hot' hydrogen is seen at higher pressures. (b) Fitting the lines requires three peaks, for 'cold' (<1 eV), 'warm' (<2.5 eV) and 'hot' hydrogen. (c) Between the electrodes in control plasmas (150 W, 0.05 Torr, H_2/Xe, 20:1) only cold and warm hydrogen are found. Away from the electrode region only cold hydrogen is present.

that the hydrogen concentration is asymmetric. For example, for the water plasmas it was consistently about twice as high at the 'pump end' (Position 3) as it is at the inlet end (Position 1, 15 cm from electrodes). Although an exhaustive study of hydrogen lines was not made at Position 1, due to the low intensity of H-atom emission at that position, a limited number of comparisons were made, and it was clear that the magnitude of the line broadening, the average excitation, and other features were very nearly identical at both ends of the cell. Another difference: most (ca. 80%) of the atomic hydrogen was 'hot' in the H_2/He plasma whereas less than half of the atomic hydrogen is found to be hot in the water plasma.

In order to obtain a measure of the average hydrogen excitation temperature (Fig. 6, and Table 6) at Positions 2 and 3 the intensities of all four Balmer lines were employed. For all of the plasmas the excitation temperature was found to be around 0.5 ± 0.1 eV (approx. 5000 ± 1000 K). This value, within the error range, was independent of the source of the magnitude of the different Balmer lines used in the computation: relative cold hydrogen intensities, relative intensities of the hot hydrogen fraction of each line, or even the relative total intensities of the Balmer lines. These values are also similar to electron temperatures measured in earlier studies of low pressure Ar plasmas generated at slightly lower powers in a large glass cavity [36]. This result suggests that the hot H is created at nearly the same location at which it is observed. Indeed, within a couple of 'mean free path' lengths, excitation temperature and kinetic temperature should be thermalized.

To further support the contention that interactions between species in the plasma leads to line broadening, a control plasma, H_2/Xe, not believed to generate broad H lines was studied in some detail in this same GEC cell. Just as in the earlier studies with H_2/He plasmas, these plasmas produced only narrow Balmer series lines (<2.5 eV) away from the electrodes whereas between the electrodes (Fig. 1C) in H_2/Xe mixtures there is some 'warm' hydrogen (<3 eV). In the earlier study, the 'control' plasma was run at pressures similar to those of the H_2/He plasma studied, about 0.5 Torr. For this study, the control plasmas were studied at pressures close to those at which selective hydrogen broadening in a water plasma was observed (<0.9 Torr). Unfortunately, even though data collection times were four times greater time periods than it was for the water plasma, Balmer series line intensity in H_2/Xe plasmas was very low, at these pressures.

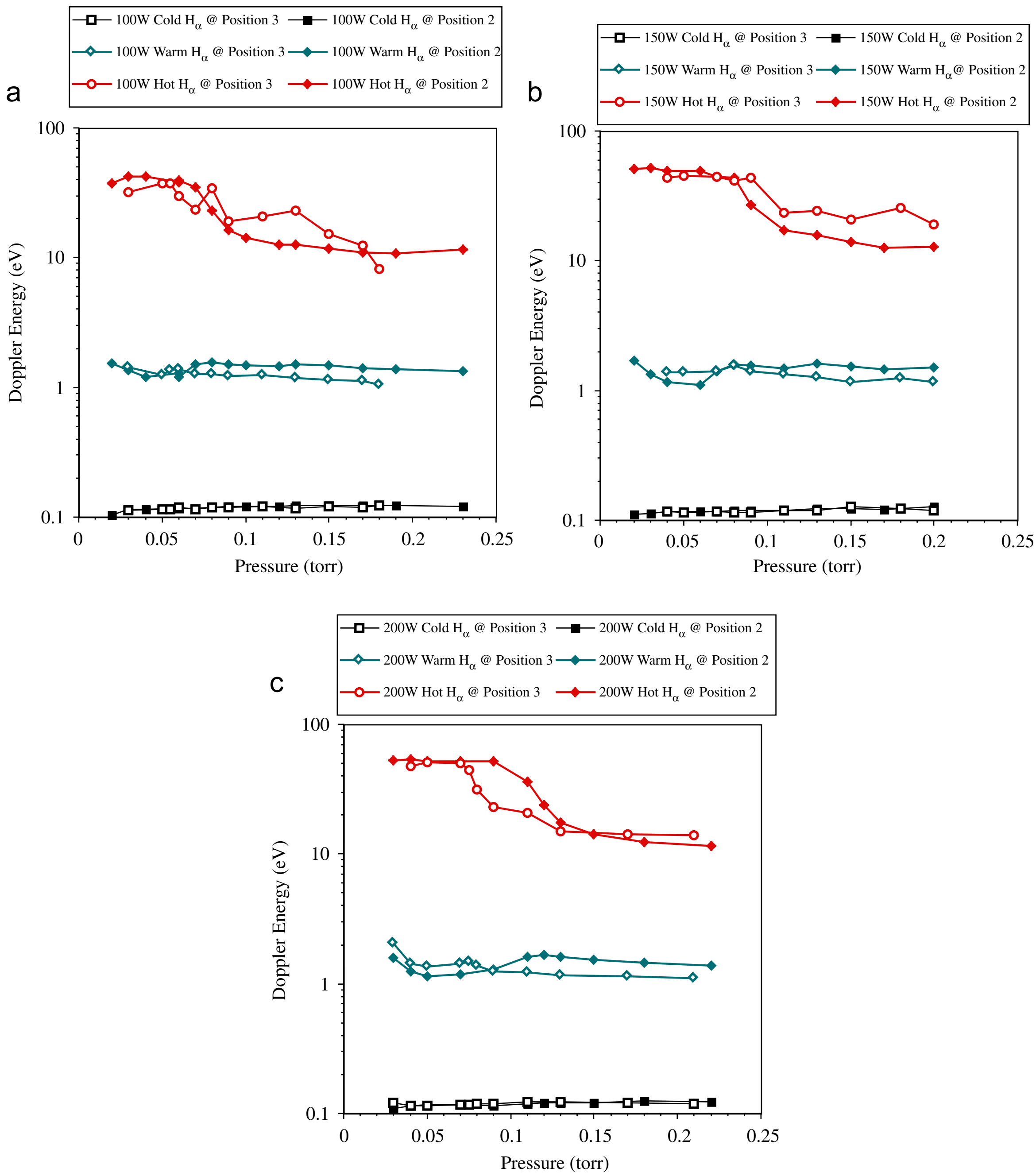

Fig. 3 – H_α broadening indicates 'hot' atomic hydrogen energy a function of pressure but not position. (a) At 100 W the broadening is approximately 40 eV up to a pressure of 0.08 Torr. (b) At 150 W the measured broadening is approximately 45 eV up to a pressure of about 0.08 Torr. (c) At 200 W the measured broadening is above 45 eV up to a pressure of nearly 0.10 Torr. In all cases the 'warm' hydrogen is less than 2 eV and the 'cold' hydrogen line width is so small it probably reflects factors (natural line width, Stark effect, instrument effects, etc.) other than Doppler broadening. Also note that the 'hot' hydrogen Doppler energy drops to between 10 and 20 eV at pressures above 0.10 Torr.

Thus, it was necessary to run nearly pure H_2 to get sufficient signal at the low pressures employed in the present work.

4. Discussion

In mixed gas plasmas containing argon and hydrogen selective line broadening of atomic hydrogen lines (no broadening of lines belonging to argon or molecular hydrogen) in high field regions [1–14] has been reported repeatedly. Even in pure hydrogen plasmas, generated with DC discharge or RF systems, including one group using a GEC cell [5], selective broadening of atomic hydrogen lines has been reported.

All groups agree that the broadening of the lines is Doppler in origin. Stark broadening can be eliminated because the

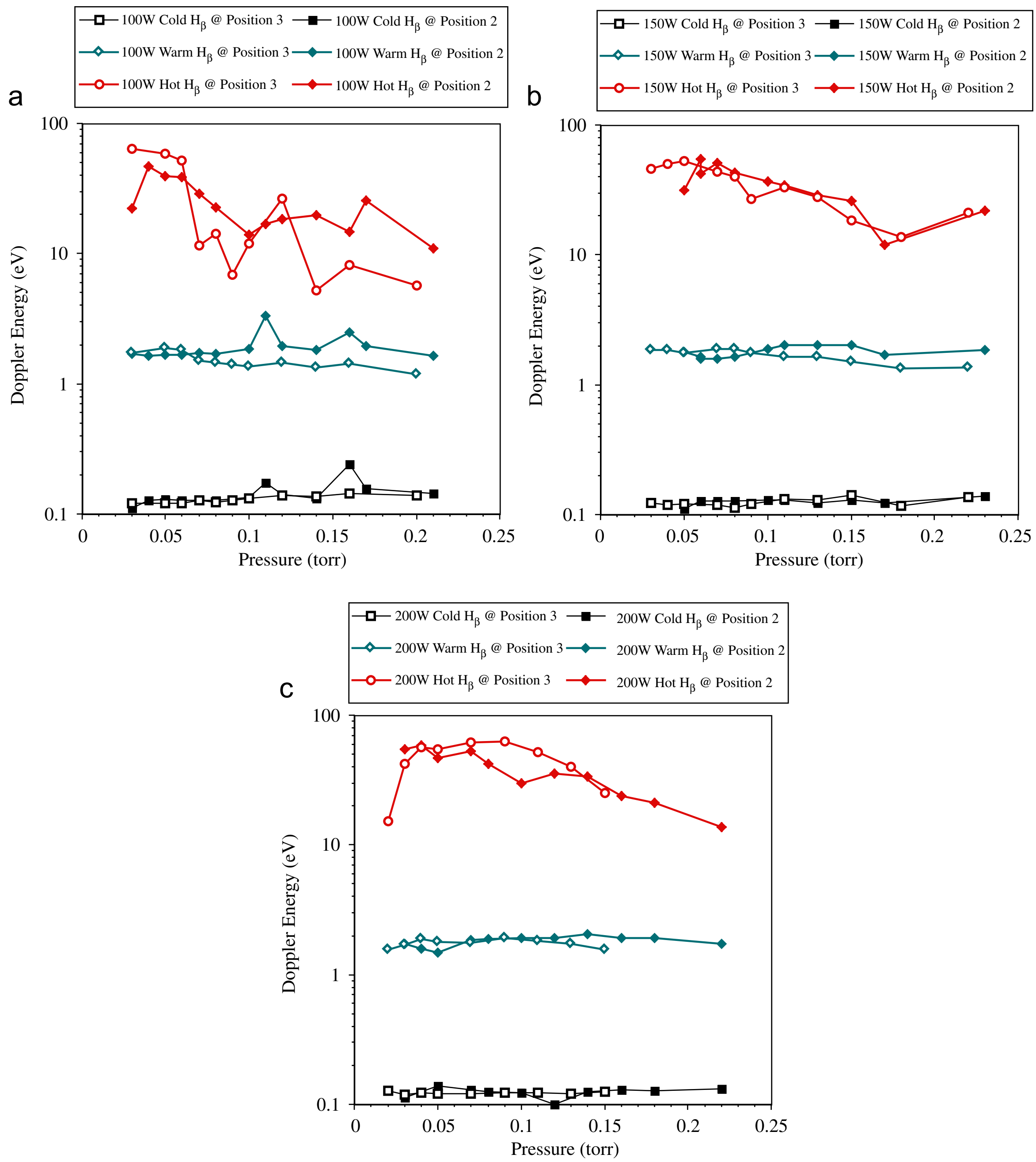

Fig. 4 – H_β broadening also indicates 'hot' atomic hydrogen energy a function of pressure but not position. (a) At 100 W the broadening is greater than 40 eV up to a pressure of 0.06 Torr. (b) At 150 W the measured broadening is greater than 40 eV up to a pressure of about 0.09 Torr. (c) At 200 W the measured broadening is above 40 eV up to a pressure of nearly 0.10 Torr. In all cases the 'warm' hydrogen is less than 2 eV and the 'cold' hydrogen line width is so small it probably reflects factors (natural line width, Stark effect, instrument effects, etc.) other than Doppler broadening. Also note that the 'hot' hydrogen Doppler energy drops to between 10 and 20 eV at pressures above 0.10 Torr.

required electron densities are orders of magnitude greater than the gas densities. Moreover, the lines are composed of three parts, hot, warm and cold. All H atoms, not just a fraction, as well as other species, would be impacted by high charge densities. Optical thickness cannot be a factor by the same argument: the entire line would be broadened, not just a fraction. Computation also shows optical thickness cannot be a factor. Specifically, for optically thin plasmas (self adsorption not significant), the value of the effective path length is less than one:

$$\tau_\omega(L) = \sigma_\omega N_H L < 1$$

where σ_ω is the cross section, N_H the number density and L is the length of plasma traversed by the signal. The value of σ_ω for Balmer α emission is $1 \times 10^{-16}\ cm^2$. An upper limit on the excited H_α density, assuming all the water is fully dissociated,

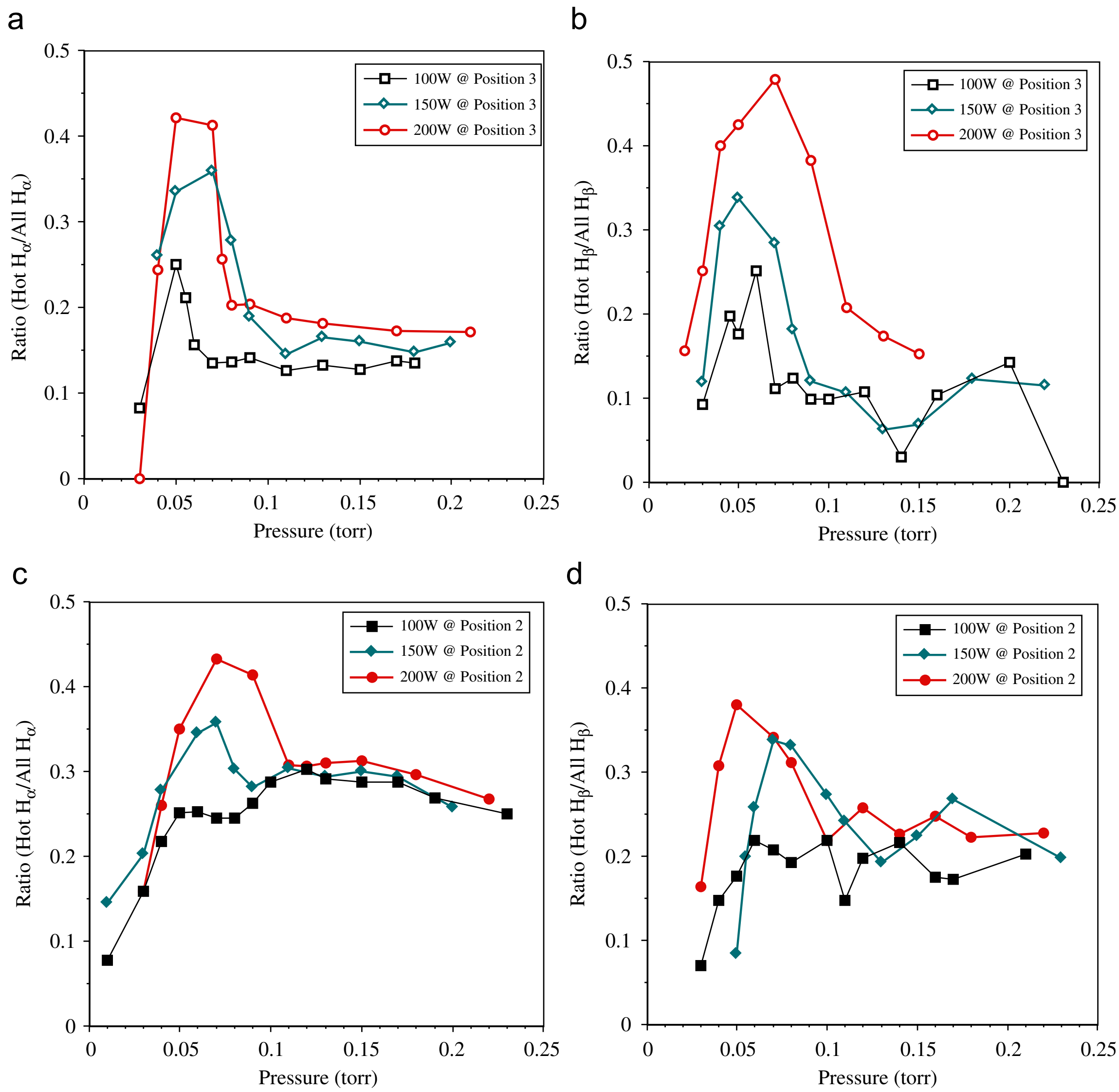

Fig. 5 – 'Hot' hydrogen between 10% and 45% of all atomic hydrogen. (a) and (b) At a position 15 cm from the electrode the fraction hot hydrogen varies as a function of pressure, and power to a lesser extent. Virtually identical trends are observed from the H_α and H_β data. (c) and (d) The trends in fraction hot hydrogen as a function of pressure and power are virtually identical between the plates and at 14 cm from the plates.

the temperature (as measured) is 5000 K, and, the excited states are populated according to the Boltzmann distribution (as measured), is 10^3 cm^{-3}. No more than 15 cm of plasma are traversed. Putting these values together yields an effective path length of the order 10^{-12}. Clearly, this plasma is optically thin. Other potential explanations, such as instrument broadening, can be readily eliminated because those mechanisms would not produce selective broadening of one species. Moreover, all the Balmer series lines are broadened, approximately to the same energy level, a result completely consistent with Doppler broadening.

All of the above arguments apply to the line broadening observed in the present work. Thus, we conclude that some of the hydrogen atoms (between 10 and 45 percent, Fig. 5) in the water plasma are selectively 'heated' to extremely high temperatures, 450,000 to 700,000 K. About half of the remaining hydrogen ('cold') produces line broadening consistent not with a Doppler effect, but rather with a combination of Stark effect, instrument effects, etc. A third type of hydrogen ('warm') may have picked up a small amount of energy from the field, possibly via one of the mechanism postulated to explain the hot atomic hydrogen found between the electrodes in H_2/Ar plasmas, as described below.

The standard physics models of generation of the hot hydrogen in H_2/Ar plasmas all include the requirement that the hydrogen ions obtain energy directly from the field [2,3]. In fact, there are two classes of models, those postulating a gas phase mechanism involving formation of hot hydrogen near the electrodes (FA), and those requiring (FA-C) that an ionic species hit the electrode, resulting in energy transfer to absorbed hydrogen species and consequently the desorption of a hot hydrogen atom [12–14]. In the gas production model a hydrogen ion, for example, H_3^+ [6], increased in concentration by interactions of H_2 with Ar, is accelerated by the field

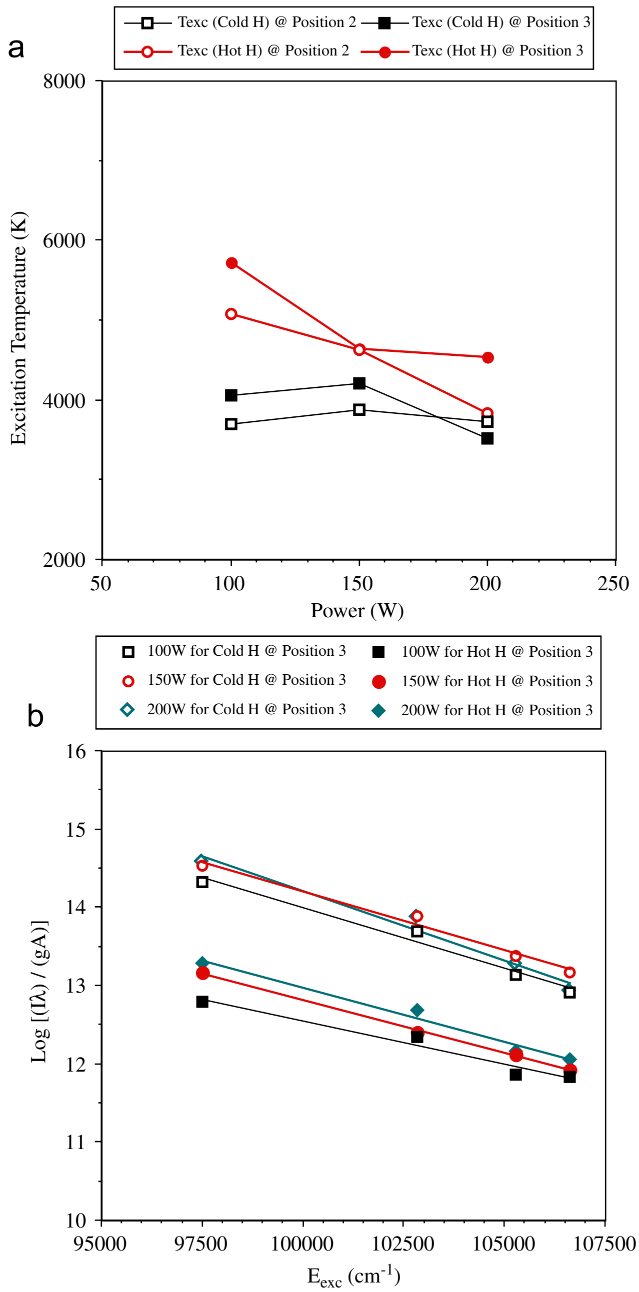

Fig. 6 – (a) Excitation energy (Tex) determined as a function of power, position and hydrogen species used to determine peak intensity. (b) Boltzman plot showing the high fidelity of the data. Clearly computing excitation temperature on the 'cold' or 'hot' component of the line intensity makes only a small difference.

toward an electrode, captures an electron via interaction with an Ar, electron dissociates to form $n=3$ state hydrogen, or forms $n=3$ state hydrogen via collision with a neutral Ar [4], and then emits. The possibility that the hot hydrogen forms from collisions with hot gas species (ions or atoms) is considered highly unlikely. First, the cross sections for collisions with H ions are too small, second spectroscopy indicates there is little or no hot argon of any form present [1,4].

In the 'bombardment' models hydrogen species on electrode surfaces are 'hit' by energized ions, generally H_3^+, H_2^+ or H^+ ions [4,6], and subsequently ejected as hot hydrogen [16,7]. In all cases, these models only predict selective hydrogen broadening in high field regions.

There does not appear to be any variation on those standard physics models capable of explaining the observations of the present work. First: hot hydrogen is found throughout the chamber, and not only in the vicinity of the electrodes. Hot hydrogen ions created near the electrodes simply cannot migrate 15 cm without equilibrating with the system. Given a maximum computation of the mean free path of 1 mm the temperature would have to remain undiminished through hundreds of collisions. The excitation temperature of the 'parent' atomic hydrogen species is only about 5000 K (approx. 0.5 eV), and as the excitation temperature of RF plasmas is generally associated with the electron temperature [37–40] this means that the internal temperature of the atomic hydrogen, as well as the temperature of the electrons in the plasma are about two orders of magnitude lower than that of the hot hydrogen. Thus, any conventional model must explain how H atoms can be two orders of magnitude hotter than the electrons in the GEC plasmas studied.

Even relatively obscure postulated processes were considered as mechanisms to provide the observed energy of the hot hydrogen atoms. For example, the 'Frank–Condon' effect [41–44] will create 'hot' neutrals with energies between 2 and 4.5 eV via wall reactions of the type:

$$H_2^+ + e^- \rightarrow 2H$$

Clearly, the energy of neutral species created in this fashion do not match the energies of the neutrals observed in this study.

In sum, it is untenable to suggest modifications of the earlier models can explain the present data. For example, all earlier models require acceleration of ions in the high field (unscreened) regions near the electrodes. They also include other specific predictions, such as preferential population of $n=3$ states, which are not observed. The gas phase models must be rejected for two additional reasons. First, they all require a high cross section for charge transfer, peculiar to argon and hydrogen ions, to allow for the rapid charge transfer necessary to create neutral, high energy H_2, which must be formed before high energy (neutral) H atoms can form. There is no argon in the plasmas studied for this work. Second, it is not plausible to suggest that the fields found 15 cm from the electrode are as strong as those found in the boundary layer near the electrodes. Plasma screening reduces the fields dramatically within millimeters. Yet, the hot hydrogen found at 15 cm from the electrodes is of the same energy as that found between the electrodes. This second objection to the gas phase models clearly also shows the 'bombardment' models to be implausible. Indeed, how can a hot hydrogen atom generated at the electrode by bombardment traverse 15 cm of the plasma without loosing energy or thermalizing? Clearly, the electrode bombardment models are not consistent with the finding of the present study that the degree of broadening is the same throughout the plasma volume. Also, we cannot identify any 'conventional physics' process that can produce hydrogen atoms with an average energy of about 45 eV for the water plasma, nearly twice the average energy observed for H_2/He plasmas generated in an identical system. Why is this process completely absent in the H_2/Xe plasmas? What 'energy from the field' process would produce neutrals with energies two orders of magnitude higher than those of the electrons in the plasma?

Given all the above objections to conventional physics we feel it is appropriate to consider very bold alternatives: The data are consistent with some predictions of the CQM theory. First, the data are consistent with a chemical reaction taking place in plasmas between species generally believed not to react chemically with each other. Second, the observations are consistent with the prediction that the reactions lead to the formation of fractional quantum state hydrogen atoms (hydrinos) with the concomitant release of energy of a large value. The consequences of this observed consistency is significant, both scientifically, and potentially technologically. From a scientific point of view the inescapable conclusion is that this and other data indicate a reason to consider the CQM theory seriously.

Strong statements such as those above would be premature in the absence of supporting evidence of numerous kinds. In fact, there is significant spectroscopic and calorimetric data already available that is consistent with these propositions. For example, the model also predicts that mixed gas plasmas will yield spectral lines of specific wavelengths in the extreme ultra-violet region of the spectrum, corresponding to the energy released in the formation of the fractional quantum states. There are several reports on spectral lines of precisely the predicted wavelengths emanating from H_2/He plasmas in the scientific literature [31,45–48]. The CQM theory even predicts the vibrational spectrum of 'hydrinos' forming molecular species, and these spectra have also been observed [49,50]. The theory also predicts that the energy released in specific mixed gas plasmas, due to the formation of fractional states of hydrogen, will be large enough to be readily measured using calorimetry. An exhaustive database exists showing that all RT plasmas do generate more energy than input to them from a microwave power supply. That is, 11 different control plasmas (e.g. Kr/H_2, N_2/H_2, Kr) were found to release almost precisely the same power into a water bath, thus defining the energy input, and this energy was 30–50% less than that produced by three (predicted) RT plasmas (H_2O, H_2/Ar and H_2/He) for the same input power [33].

The theory also predicts that a discharge across/through a gas phase is not required to produce the reactions leading to the production of fractional quantum states. Consistent with this prediction of the theory are reports from several labs of 'thermal' plasmas [44]. That is, bright, discharge like, 'plasmas' created without an electric discharge in gaseous environments containing H atoms and (predicted) appropriate 'catalytic' species. The same systems with chemically similar, but non-catalytic species replacing the catalytic species, are dark. There is absolutely no evidence of plasma like discharges.

According to CQM theory two body reactions capable of producing the observed energies from an oxygen catalyst include these:

$$O_2 + H \rightarrow H(1/3) + O + O^{2+} + 54.4\,eV \quad (1)$$

and

$$O_2 + H \rightarrow H(1/4) + O + O^{3+} + 108.8\,eV \quad (2)$$

The notation '$H(1/n)$' describes smaller forms of hydrogen in the CQM theory [28,29,45]. Indeed, in that theory, electrons are real particles, shaped like hollow spheres of charge, with absolute dimensions, including radius. Specifically, a hydrino of form $H(1/n)$ can be described to a first approximation as a hollow, 'spherical bubble' of charge, obeying Newtonian mechanics and Maxwell equations, symmetrically surrounding the atomic nucleus with a radius equal to a_0/n, where a_0 is the Bohr radius. As discussed elsewhere [1] the energy released by these reactions can be released as a photon, or as kinetic energy. In the latter case, it is also clear momentum must be conserved. As oxygen is far more massive than hydrogen, or hydrino, most of the energy released is with the hydrino.

Hydrinos do not produce Balmer lines. Some mechanism of energy transfer from the hydrino to atomic hydrogen must be suggested. Subsequent to the formation of the hydrino, it can collide with atomic hydrogen to produce hot hydrogen, with an energy less than or equal to that of the hydrino:

$$H(1/n)\,\underline{E1} + H \rightarrow H(1/n)x\,\underline{E1} + H(1-x)\,\underline{E1} \quad (3)$$

In this equation $\underline{E1}$ represents the energy of the hot hydrino (e.g. Eq. (1)), and x is the fraction of the energy that is not lost by the hydrino in a momentum conserving collision with a hydrogen atom. In a 'head-on' collision of two equal masses, x will go to zero. On this basis, it is clear hydrinos formed via Rxns (1) can generate H atoms with energies as high as 54.4 eV and hydrinos formed via Rxn (2) can create hydrogen atoms with energy greater than 100 eV.

Based on the energies observed in this study it appears that Rxn (1) is more common than Rxn (2), but in some cases some of Rxn (2) must occur. In some cases it is clear (see tables) that H atoms with an 'average' energy (assuming random orientation and Boltzmann energy distribution) of more than 60 eV. Why do not we observe other line broadening, for example 'warm' atomic oxygen? Clearly, if momentum is to be conserved, virtually all the energy in a collision between a hot hydrino remains with the hydrino. Still, a concomitant consideration of energy/momentum conservation indicates an oxygen atom will pick up as much as 10% of the total energy during a 'head-on' collision with a 'hot hydrino'. This suggests O atoms with energy in the 5 eV range might predictably be expected. There is a need for additional studies, for example, solely of the O atom spectra in an RF generated water plasma, such as the current one, to provide more detailed answers.

There are a host of other processes that also lead to an energy transfer to H atoms. For example, there is a process predicted by CQM called 'disproportionation' [1,28,29,45]. A typical disproportionation process purported to create hot H atoms:

$$H(1/2) + H(1/2) \rightarrow H + H(1/3) + 27.2\,eV \quad (4)$$

This reaction, because of the need to conserve momentum and energy, would produce an H atom with 13.6 eV of energy.

It is informative to compare the catalytic reactions predicted by CQM to occur in Ar/H_2 and He/H_2 plasmas with those described above for a helium plasma. In an Ar/H_2 plasmas the only two body reaction that produces hydrinos is as follows:

$$H + Ar^{+} \rightarrow H(1/2) + Ar^{2+} + 13.6\,eV \quad (5)$$

In a helium plasma, this reaction is predicted:

$$H + He^{+} \rightarrow H(1/3) + He^{2+} + 54.4\,eV \quad (6)$$

Looking at these reactions it is reasonable to expect a gross 'order' of energy level prediction from the three types of RF plasmas investigated to date. That is, in each system a number of different processes are purportedly taking place, hence a single and absolute energy is not predicted. Yet, it is reasonable to postulate that the relative magnitude of average broadening in nearly identical plasma systems will increase with the amount of energy released by the chief catalytic reactions. According to this postulate, the energy should go in this order: $Ar/H_2 < He/H_2 < H_2O$, In fact, this is in agreement with observation [1,15], hence a consideration of the degree of broadening also fails to disprove the CQM theory.

Including this report there are now at least four reports of dramatic H atom line broadening in RT plasmas [1,15,16,51]. Also, reports have been submitted which demonstrate conclusively that the 'product gases' of RT plasmas have unique chromatographic [52], NMR signatures [53], EUV [30,44–48] and even excess heat [33] signatures consistent with the behaviors expected according to the CQM model. Moreover, the data generated from a host of Balmer line broadening studies in other labs is consistent with CQM theory.

Given this information, it is entirely within the realm of the scientific process to make these bold suggestions. Indeed, we believe, after Popper [54], that following the scientific process requires constantly attempting to disprove ('falsify'), empirically, the theory under consideration. Each failure to produce a negative result increases the 'degree of corroboration'. We believe that the 'degree of corroboration' which 'increases with the number of corroborating instances' is sufficient to merit open discussion of the very new ideas of quantum mechanics presented by Mills.

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