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Spatially Resolved Optical Emission and Modelling Studies of Microwave-Activated Hydrogen Plasmas Operating under Conditions Relevant for Diamond Chemical Vapor Deposition

Edward J.D. Mahoney,^{1,2} Benjamin S. Truscott,^{1,a} Sohail Mushtaq,¹ Michael N.R. Ashfold,^{1*} and Yuri A. Mankelevich³

¹ School of Chemistry, University of Bristol, Bristol, U.K. BS8 1TS

² Centre for Doctoral Training in Diamond Science and Technology, University of Warwick, Gibbet Hill Road, Coventry, U.K., CV4 7AL

³ Skobel'tsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Leninskie gory, Moscow, 119991 Russia

^a Present address: Element Six Global Innovation Centre, Harwell Campus, Fermi Ave, Didcot, U.K., OX11 0QR

Abstract

A microwave (MW) activated hydrogen plasma operating under conditions relevant to contemporary diamond chemical vapour deposition reactors has been investigated using a combination of experiment and self-consistent 2-D modeling. The experimental study returns spatially and wavelength resolved optical emission spectra of the d→a (Fulcher), G→B and e→a emissions of molecular hydrogen and of the Balmer- α emission of atomic hydrogen, as functions of pressure, applied MW power and substrate diameter. The modeling contains specific blocks devoted to calculating (i) the MW electromagnetic fields (using Maxwell's equations) self-consistently with (ii) the plasma chemistry and electron kinetics, (iii) heat and species transfer, and (iv) gas-surface interactions. Comparing the experimental and model outputs allows characterization of the dominant plasma (and plasma emission) generation mechanisms, identifies important coupling reactions between hydrogen atoms and molecules (*e.g.* the quenching of $H(n > 2)$ atoms and electronically excited H_2 molecules (H_2^*) by the alternate ground state species, and H_3^+ ion formation by the associative ionization reaction of $H(n = 2)$ atoms with H_2) and illustrates how spatially resolved H_2^* (and H_α) emission measurements offer a detailed and sensitive probe of the hyperthermal component of the electron energy distribution function.

1. Introduction

A recent article in a collection commemorating the 150th anniversary of the death of Michael Faraday¹ highlighted the numerous studies that have used optical emission spectroscopy (OES) methods to investigate the microwave (MW) plasma assisted (PA) chemical vapour deposition (CVD) of diamond. Most high-quality CVD diamond is grown from process gas mixtures containing a small percentage of methane in hydrogen.^{2,3} Yet, despite the dominance of H₂ in the process gas, relatively few OES studies of the diamond CVD environment have focussed on the information that could be provided by analysis of the H₂ emissions.⁴⁻⁸

H₂ shows a wealth of rovibrational structure in the visible and near infrared (IR) spectral regions associated with transitions between bound excited electronic states.⁹⁻¹¹ Most prior experimental studies of MW activated hydrogen-containing plasmas have focussed on the d³Π_u–a³Σ_g⁺ (Fulcher) system,^{5-6,7,8,12-28} though lines within the G¹Σ_g⁺–B¹Σ_u⁺ origin band 5–67 and a³Σ_g⁺–b³Σ_u⁺ continuum emission^{27,28} have been used for plasma diagnostics and limited studies have been undertaken using the e³Σ_u⁺–a³Σ_g⁺ system.²⁹ As Figure 1 shows, the structured emissions are from excited states that lie at energies >13 eV above the ground (X¹Σ_g⁺) state of H₂. These emissions have been used to estimate H₂ rotational and vibrational temperatures (T_{rot} and T_{vib} , respectively), to probe electron energy distribution functions (EEDFs) and electron temperatures, T_e , and to infer the degree of H₂ dissociation, with – on occasion – some spatial resolution within the plasma volume and/or as functions of process conditions (pressure, MW power density, *etc*). Such data have helped inform the development of physicochemical models for diamond growth.^{25-27,30-32} But Figure 1 also illustrates some of the challenges associated with any detailed study of these H₂ emissions. The excited state density is high, and many of the emitting levels are perturbed by interaction with other close-lying energy levels. Analysis is further complicated by the accidental overlap of spectral lines,^{9-11,33} which is exacerbated by the high (~3000 K) gas temperature in the plasma core^{1,34} which increases both the number and the widths (via Doppler broadening) of the emission lines.

The literature also contains many prior theoretical studies of H₂ plasmas, including moderate pressure MW-activated H₂ plasmas.^{24-26,30,32,34-43} As the present work demonstrates, however, a complete understanding of the various processes and effects in such H₂ plasmas, with and

without the hydrocarbon additions required for diamond CVD, remains elusive. There is also a wealth of published data pertaining to electron-hydrogen collision cross-sections, ranging from the early study of Engelhardt and Phelps⁴⁴ through to recent experimental studies⁴⁵⁻⁴⁹ and reviews.⁵⁰⁻⁵³ These data contain contradictions, however, and for many basic processes (*e.g.* associative ionization in the reactions of $H(n > 1)$ atoms with H_2 molecules and with H atoms, the relationship between such processes and electron impact ionization of H_2 and H , and the collisional quenching of $H(n > 1)$ atoms and/or electronically excited H_2^* molecules, *etc.*) there appears still to be no clear consensus view.

The present work seeks to resolve some of these controversies and to characterize the dominant plasma and plasma emission generation mechanisms prevailing in MW-activated H_2 plasmas operating under conditions relevant to contemporary diamond CVD reactors using a combination of experiment and theory. The experimental data comprise spatially resolved OES from selected levels of three different excited electronic states of H_2 (the $d^3\Pi_u$, $G^1\Sigma_g^+$ and $e^3\Sigma_u^+$ states, monitored via the d-a (Fulcher), G-B and e-a transitions, respectively) and from the $n = 3$ level of atomic hydrogen (via the Balmer- α emission), as functions of three experimental variables: pressure, p , applied MW power, P , and substrate diameter, d_{sub} . These data are compared and contrasted with the outputs of a new self-consistent two-dimensional (2-D (r, z)) model of the various plasma-chemical, transport and electromagnetic processes. r and z are, respectively, the radial distance and the vertical height from the center of the substrate surface which defines $r = z = 0$. Such comparisons serve to highlight important coupling reactions between hydrogen atoms and molecules (*e.g.* the quenching of $H(n > 2)$ atoms by H_2 and of H_2^* molecules by $H(n = 1)$ atoms, and the associative ionization of $H(n = 2)$ atoms with H_2). They also demonstrate how measurements of H_2^* emissions can offer a more sensitive probe of the hyperthermal component of the EEDF and its spatial variation than the (more traditionally monitored) H^* emissions. Companion studies exploring additional effects caused by the addition of noble gas (Ar or Kr) to a hydrogen plasma are reserved for a future publication.

2. Experimental

The experiment employed upgraded versions of our previously described custom designed MW PACVD reactor⁵⁴ and optical emission imaging setup.⁵⁵ One key upgrade to the former is the way that process gas is introduced at the top of the reactor. The previous two diametrically opposed inlet pipes have been replaced by eight symmetrically arranged 4 mm

inlets in order that the input gas flow better approximates the cylindrical symmetry assumed in the modelling. Base plasma conditions for the present study were: $p = 150$ Torr, $P = 1.5$ kW, and a H_2 flow rate $F(H_2) = 300$ standard cm^3 per minute (sccm).

The present study employed 3 mm thick cylindrical tungsten substrates of three different diameters. These were mounted axi-symmetrically, on an annular spacer (molybdenum wire) on a new and improved water-cooled reactor base plate. The latter comprises an oxygen-free electronic grade copper (UNS code C10100) sample stage mounted in a 6082 aluminium alloy base. The diameter of the spacer wire (and the gas gap it creates) determines the thermal conduction from the substrate to the base plate and thus offers crude control of the substrate temperature, T_{sub} . Base conditions employed a substrate with diameter $d_{\text{sub}} = 32$ mm (radius $R_{\text{sub}} = 16$ mm) and a spacer wire with diameter, $d_{\text{wire}} = 0.01$ ". The substrate temperature T_{sub} under these conditions was ~ 700 °C, as measured using a two-colour pyrometer (700–2400 °C, Landmark X model LMX V1.14) or inferred from one-colour pyrometer measurements (600–900 °C, Agema model TPSXHHTCF2). The effects on the plasma of changing input power and H_2 pressure while operating with this base substrate were investigated over the ranges $0.7 \leq P \leq 1.85$ kW and $50 \leq p \leq 275$ Torr. Standard operating practice dictated that, while varying one parameter, the others were maintained at their base values.

A more limited set of experiments were undertaken with two other W substrates, of the same thickness, with $d_{\text{sub}} = 27$ mm and 17 mm. Emissions from plasmas operating with both substrates and spacers with $d_{\text{wire}} = 0.01$ " were measured for base conditions (*i.e.* $p = 150$ Torr, $P = 1.5$ kW). Emissions were also measured for the $d_{\text{sub}} = 17$ mm substrate mounted on a thinner spacer wire ($d_{\text{wire}} = 0.004$ "") for $P = 0.9, 1.5$ and 1.85 kW, and $p = 75, 150$ and 275 Torr. Exchanging substrates and/or spacer wires required frequent opening and re-evacuation of the reactor, so it was prudent to quantify the air leak rate periodically by measuring the pressure rise (from base vacuum) over a fixed period of time. Typical leak rates during the present data collection were ~ 0.002 torr min^{-1} (which would translate into an air impurity of ~ 25 ppm at the base flow rate and pressure).

Optical emission from the plasma was monitored using a Czerny-Turner spectrograph (Shamrock SR-500i) with a 50 mm focal length, f/16 objective lens. The H_2^* emissions were dispersed using a 700 grooves mm^{-1} grating (a 400 grooves mm^{-1} grating was used for the H_α measurements) and detected on a cooled CCD detector (Andor Newton 940) with an overall spatial magnification of ~ 0.08 . This choice of grating yielded a spectral resolution of ~ 0.04

nm (≈ 0.06 nm for the H_α measurements) when using a 10 μ m entrance slit, and a spatial (vertical) resolution better than 0.5 mm. Each H_2^* and H^* image was accumulated for (or scaled to an equivalent accumulation time of) 640 s and, given the small lens aperture employed, is assumed to include emission from the entire depth of the plasma (*i.e.* are best viewed as column integrated line intensities).

3. Results and Discussion

3.1 Experimental results

The experiments return wavelength (λ) and spatially (z) resolved column integrated intensities $I_{\text{em}}(\lambda, z)$ of the d–a, G–B and e–a emissions of H_2 and the H_α emission at 656 nm. Most previous H_2 emission studies have focussed on the richly structured (but, from a spectroscopic perspective, still quite poorly characterised) d–a Fulcher band system in the visible red region of the electromagnetic spectrum. The sensitivity of contemporary CCD detectors now extends well into the near IR region, however, and the spectrally simpler e–a system offers an attractive alternative. The H_2 data shown in this paper are derived from e–a emission measurements unless stated otherwise. Figure 2(a) shows an illustrative $I_{\text{em}}(\lambda, z)$ image of the H_2 (e–a) emission recorded under base conditions, after post-processing to correct for a small vertical skew in the underpinning raw data. Similar $I_{\text{em}}(\lambda, z)$ images were recorded for the other H_2^* emission systems and are shown in Figs. S1 and S2 of the Supplementary Information. The vertical axis in Fig. 2(a) corresponds to height z relative to the upper surface of the substrate and ranges from $-3 \leq z \leq 27$ mm, with $z = 0$ defining the surface; the scale is calibrated by imaging a test target placed at the substrate centre.

Figure 2(b) shows the intensities of individual emissions (summed over the range $3 \leq z \leq 6$ mm) plotted as a function of wavelength. These features can all be identified from the line listing in ref. 9; R branch lines in the H_2 (e–a) (0–0) band up to R(9) (*i.e.* the $J'=10 \rightarrow J''=9$ transition) are indicated in the figure, though the analysis that follows makes use of all features extending out to the R(11) line at 881.7 nm. The 3:1 odd:even J'' intensity alternation – reflecting the spin statistics associated with the two identical $I = \frac{1}{2}$ nuclei – is clearly evident in the spectrum, but the relative line intensities are also sensitive to local spectroscopic perturbations (currently under investigation) and the wavelength dependent spectrometer response function (which has not been applied to the current data). At this time, therefore, we do not attempt a quantitative determination of rotational temperatures, T_{rot} , (and

thus, by extension, the local gas temperature, T_g) from emission spectra such as that shown in Figure 2(b). In the context of diamond CVD, there is no need: many prior studies of activated dilute CH_4/H_2 gas mixtures have demonstrated that T_{rot} values derived from analysis of the emission (and absorption) spectra of C_2 and/or CH radicals can provide a reliable measure of T_g in the hot plasma region.³ Nonetheless, we note that the measured intensity ratio of the $\text{R}(9):\text{R}(1)$ lines of the $\text{H}_2(\text{e}-\text{a})$ (0-0) band, for example, increases with increasing z (from 0.66 in the range $0 \leq z \leq 1.5$ mm to 0.93 at $6 \leq z \leq 7.5$ mm), consistent with the increase in T_g on moving from the substrate towards the plasma core predicted by prior modelling at these base p and P conditions.³¹

We now focus on the spatial distributions of the H_2^* and H_α emissions, and how these vary with changes in process conditions. Figure 3 compares the $I_{\text{em}}(z)$ distributions of the three different H_2^* emissions recorded under base conditions. The distributions of e-a emission reported here and in Figures 4 and 5 were obtained by summing the intensities of the $\text{R}(0)-\text{R}(11)$ lines in the (0,0) band, while the d-a intensities reported in Figure 3 and in Figures 6 and 7 (and the G-B intensities reported in Figure 3) were obtained by summing the intensities of the starred and identified lines in Figures S1 and S2. The three $I_{\text{em}}(\text{H}_2^*)$ vs. z distributions are reassuringly similar: all peak at $z \sim 2.6$ mm and fall to near-zero intensity by $z \sim 20$ mm, and are very different from the $I_{\text{em}}(\text{H}_\alpha)$ distribution which, as reported previously,⁵⁶ peaks at $z \sim 7.5$ mm and similarly extends to $z \sim 20$ mm under base conditions of p and P . The spatial profiles in Figure 3 show the data prior to any smoothing and are color coded to match the respective transitions in Figure 1. The spatial profiles shown subsequently (*i.e.* Figure 4 onwards), in contrast, have had a Savitzky-Golay smoothing applied where appropriate.

Figures 4 and 5 show how the $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ distributions vary with, respectively, P and p . Focussing first on variations with MW power, Figure 4(a) shows that the $I_{\text{em}}(\text{H}_2^*)$ distribution recorded at $P = 0.7$ kW and base p (150 Torr) and d_{sub} (32 mm) peaks at $z \sim 6$ mm and is noticeably narrower (with a full width half maximum (FWHM) of ~ 10 mm) than those shown in Figure 3. Upon increasing P , the $I_{\text{em}}(\text{H}_2^*)$ distribution soon extends to $z \sim 20$ mm, progressively gains intensity at small z but is relatively constant in the plasma centre. These changes can be seen more clearly in Figure 4(c), which shows how the summed $I_{\text{em}}(\text{H}_2^*)$ intensities in the ranges $z = 2.25 \pm 0.75$ mm and $z = 8.25 \pm 0.75$ mm vary as a function of P . The 2.5-fold increase in P (from 0.7 to 1.85 kW) causes a linear ~ 6 -fold increase in $I_{\text{em}}(\text{H}_2^*)$ at low z but only a very small monotonic decrease in $I_{\text{em}}(\text{H}_2^*)$ in the centre of the plasma.

Figure 4(b) shows the $I_{\text{em}}(\text{H}_\alpha)$ distribution measured at $P = 0.7$ kW peaking at $z \sim 7.5$ mm. Increasing P leads to increased $I_{\text{em}}(\text{H}_\alpha)$ intensity at all z , an expansion of the $I_{\text{em}}(\text{H}_\alpha)$ distribution in z , and the progressive appearance of a shoulder at smaller z . Figure 4(c) shows a near linear ~ 7 -fold increase in $I_{\text{em}}(\text{H}_\alpha)$ in the range $z = 2.25 \pm 0.75$ mm upon increasing P from 0.7 to 1.85 kW; this same 2.5-fold increase in P causes a somewhat smaller (~ 5 -fold), less than linear, increase in $I_{\text{em}}(\text{H}_\alpha)$ in the range $z = 8.25 \pm 0.75$ mm. These changes in P inevitably also have some influence on T_{sub} , which was below the detection limit at $P = 0.7$ kW, ~ 700 °C at $P = 1.5$ kW and ~ 810 °C at $P = 1.85$ kW.

$I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ respond very differently to changes in p . Figure 5(a) shows that $I_{\text{em}}(\text{H}_2^*)$ is greatest and that the $I_{\text{em}}(\text{H}_2^*)$ distribution is most extensive at $p = 50$ Torr (with base P (1.5 kW) and d_{sub} (32 mm)). Increasing p from 50 to 275 Torr causes a contraction of the distribution at large z and a gradual ~ 4 -fold reduction in the maximum value of $I_{\text{em}}(\text{H}_2^*)$. The peak of the distribution is at $z \sim 4$ mm at low p (50 Torr), reduces to $z \sim 2.5$ mm by $p = 150$ Torr but then reverts to $z \sim 4$ mm at $p = 275$ Torr – by which pressure the low z contribution has disappeared. Figure 5(c) shows these trends more explicitly. The summed $I_{\text{em}}(\text{H}_2^*)$ intensities in the ranges $z = 2.25 \pm 0.75$ mm and $z = 8.25 \pm 0.75$ mm both follow a $\sim 1/p$ dependence once p exceeds ~ 100 Torr. The $I_{\text{em}}(\text{H}_\alpha)$ distribution is also broadest at low p and narrows with increasing p but the summed $I_{\text{em}}(\text{H}_\alpha)$ intensities in the lower and higher z ranges appear to saturate at higher p . T_{sub} was below our detection limit at $p = 50$ Torr, but in this set of experiments had increased to ~ 650 °C at $p = 150$ Torr and ~ 690 °C at $p = 275$ Torr (as inferred from the one-color pyrometer measurements).

The third variable in the present experiment was d_{sub} which, as Figures 6(a) and 6(b) show, has a dramatic effect on the $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ distributions. The obvious changes in the $I_{\text{em}}(\text{H}_2^*)$ distribution upon reducing d_{sub} from 32 to 17 mm (with all other parameters held at their base values) are at small z , where ‘additional’ emission centred close to $z \sim 0$ mm dominates in the case of small d_{sub} . Two colour pyrometer measurements of the substrate temperature (listed in the caption to Figure 6) show an obvious anti-correlation between T_{sub} and d_{sub} . The corresponding $I_{\text{em}}(\text{H}_\alpha)$ distributions reveal a modest increase in the peak $I_{\text{em}}(\text{H}_\alpha)$ value in the plasma core upon reducing d_{sub} but, again, this is overshadowed by the emergence of a second feature centred at $z \sim 0$ mm. The $d_{\text{sub}} = 17$ mm substrate is visibly red hot under these conditions, with a luminous halo extending from the circumference to $z < 0$.

The $z \sim 0$ emission features can be suppressed by operating at higher p , lower P or lower T_{sub} . Figure 7 shows $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ distributions determined for plasmas operating at $p = 75$, 150 and 275 Torr and $P = 1.5$ kW using the $d_{\text{sub}} = 17$ mm substrate and a thinner spacer wire ($d_{\text{wire}} = 0.004''$), i.e. at lower T_{sub} . The appearance of the plasma changes with p . As shown in the inset to Figure 7(b), the aforementioned luminous halo is clearly visible at $p = 75$ Torr, is brighter at 150 Torr but by 275 Torr has been replaced by an emission that is concentrated above the substrate centre. The T_{sub} values in this case were below the detection limit at $p = 75$ Torr, increasing to ~ 910 °C at $p = 150$ Torr (*cf.* 1315 °C when using $d_{\text{wire}} = 0.01''$, Figure 6) and ~ 940 °C at $p = 275$ Torr. As Figure 7 shows, the $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ distributions are again most extensive and most obviously bimodal at low p but, comparing the $p = 150$ Torr data in Figures 6 and 7, it is clear that the ‘peak’ (*i.e.* $z \sim 0$) to ‘tail’ ($z \gg 0$) intensity ratios for both $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ are smaller when using the thinner d_{wire} (*i.e.* lower T_{sub}). With increasing p , both distributions shrink in spatial extent. $I_{\text{em}}(\text{H}_2^*)$ decreases with increasing p . $I_{\text{em}}(\text{H}_\alpha)$, in contrast, increases upon raising p from 75 to 150 Torr but declines upon further increases in p , and the peak of the $I_{\text{em}}(\text{H}_\alpha)$ distribution shifts to smaller z . Analogous data taken at $P = 0.9$ kW and 1.85 kW demonstrate broadly similar trends (Figures S3 and S4, respectively).

3.2 Modelling the MW activated H₂ plasma

The present study required a significant advance of our previously reported 2-D(r, z) model of MW plasma processes. Specifically, the previous model containing specific blocks devoted to plasma-chemical and electron kinetics, heat and species transfer, and gas-surface interactions,³¹ was enhanced by introducing an additional block wherein Maxwell’s equations are used to calculate the MW electromagnetic fields self-consistently with the plasma chemistry and electron kinetics. This section describes these extensions and the application of the extended 2-D self-consistent model to MW activated H₂ plasmas. Comparing the extended model outputs with the spatially resolved OES data recorded at different p and P then allows investigation of the sources and sinks of H($n = 2, 3$) atoms and of H₂* excited states and identification of the most important production and loss reactions for these species, largely on the basis of experimentally derived reaction rate coefficients. Base conditions for the modeling are as close as possible to those used in the experimental study: $p = 150$ Torr, $P = 1.5$ kW, H₂ gas with a 25 ppm air impurity (*i.e.* 5 ppm O₂). Oxygen is converted to H₂O

under the prevailing reactor conditions (*i.e.* high T_g and H atom mole fraction). The main effect of this level of O_2 contamination is to convert more than half of the H_3^+ (which would be the dominant ion in a pure H_2 plasma under the present conditions) into H_3O^+ ions via the proton transfer reaction $H_3^+ + H_2O \rightarrow H_3O^+ + H_2$ (which is exothermic by ~ 1.8 eV⁵⁷). The present study suggests that changing the dominant ion in the plasma core from H_3O^+ (as in an H_2 plasma operating under the present base conditions) to H_3^+ (as in an H_2 plasma containing much less, or zero, air impurity) reduces the electron-ion recombination rate, but has no significant impact on the MW electric fields or neutral species concentrations. For example, reducing the air impurity from 25 ppm to 5 ppm is predicted to cause a modest (few %) reduction in the electric fields in the plasma core. In both cases, however, H_3O^+ remains a dominant ion outside the plasma core, where the $H_3O^+ + e$ dissociative recombination reaction determines the electron number density and the MW power absorption.

Any air impurity necessarily implies the presence of nitrogen also. In the present context, the most important charge transfer reactions involving the main nitrogen containing contaminants are $H_3^+ + N_2 \leftrightarrow N_2H^+ + H_2$ and $H_3^+ + NH_3 \leftrightarrow NH_4^+ + H_2$. The exothermicity of the former reaction is only ~ 0.5 eV, which moderates the N_2H^+ concentration and ensures that $[N_2H^+] \ll [H_3^+]$. The latter reaction, in contrast, is highly exothermic (~ 4.5 eV). Thus the reverse reaction is an insignificant destruction route for NH_4^+ ions, but the NH_4^+ concentration is limited by the low NH_3 concentration ($[NH_3] \ll [N_2]$ under the relevant process conditions⁶⁰) and by the efficiency of the $NH_4^+ + e$ dissociative recombination reaction. 2-D model calculations for a 20 ppm N_2 in H_2 mixture return $[N_2H^+]$ and $[NH_4^+]$ values $< 10^9$ cm⁻³ (*cf.* $[H_3^+] > 10^{11}$ cm⁻³ and $[H_3O^+] \sim 10^{11}$ cm⁻³), justifying our neglect of specific reference to the effects of the N_2 contaminant.

3.2.1 A self-consistent 2-D model of the MW activated H_2 plasma

As before,³¹ the Boltzmann kinetic equations have been solved numerically for a range of plasma conditions with proper inclusion of detailed balance of the electron impact induced excitation and de-excitation of the various rotational and vibrational levels of H_2 in order to obtain realistic EEDFs and rate coefficients for all important electron impact induced processes under study. The various electron rate coefficients k_i are calculated by integrating the corresponding electron reaction cross-sections with the local $f(\epsilon)$ functions, which depend on the following local parameters: the reduced electric field, $|E|/(N \times a)$, the gas temperature, T_g , the mole fraction of H($n = 1$) atoms, X_H , and the rovibrational (v, J) level populations in

the ground (X) state H_2 molecules.³¹ $|E|$ is an absolute value of the electric field averaged over the MW period, N is the gas concentration, and the factor $a = (1 + \omega^2/\nu^2)^{0.5}$, where $\omega = 2\pi f$ (with $f = 2.45 \times 10^9 \text{ s}^{-1}$) and ν are the MW and electron collision frequencies, respectively. The ω/ν ratios for the present plasma conditions were varied over the range $0.05 < \omega/\nu < 0.7$.

Figure 8 shows normalized EEDFs, $f(\epsilon)/n_e$ (where $n_e = \int f(\epsilon) d\epsilon$ is the electron concentration), for five different plasma conditions (*i.e.* conditions defined by five different combinations of $|E|/(N \times a)$, X_H and T_g). These EEDFs each show two temperature components and have the general form $f(\epsilon) = c_1 \times \exp(-\epsilon/T_1)$ for the energy range $2 < \epsilon < 10.2 \text{ eV}$ and $f(\epsilon) = c_2 \times \exp(-\epsilon/T_{\text{tail}})$ for $\epsilon \geq 10.2 \text{ eV}$. The high energy tail and average electron temperatures (T_{tail} and T_e) in each case are detailed in the caption to Figure 8. The former is defined by the slope of the EEDF at $\epsilon > 10.2 \text{ eV}$, while the average electron temperature $T_e = 2\epsilon_{\text{av}}/3$ is determined by the average electron energy, $\epsilon_{\text{av}} = \int \epsilon f(\epsilon) d\epsilon / \int f(\epsilon) d\epsilon$.

The EEDFs established by the electromagnetic fields and by absorption of MW power by the electrons in the collisional plasma environment determine the spatial distributions of the source and loss terms for the active particles within the plasma. Of particular relevance to the current study, the $f(\epsilon) = c_2(|E|/(N \times a), T_g, X_H) \times \exp(-\epsilon/T_{\text{tail}})$ component determines the production rates of species like $H(n > 1)$ and H_2^* with excitation thresholds $E_i \geq 10.2 \text{ eV}$. Thus we have calculated EEDFs for a 3-D array of $|E|/(N \times a)$, X_H and T_g parameters in order to determine process-dependent rate coefficients $k_i = \int v \sigma_i(\epsilon) f(\epsilon) d\epsilon / \int f(\epsilon) d\epsilon$, where $v = (2\epsilon/m_e)^{0.5}$ and m_e are the electron velocity and mass, respectively, and $\sigma_i(\epsilon)$ is the cross-section for process i . Analysis of these calculated results shows that the coefficients $k_i [\text{cm}^3 \text{ s}^{-1}]$ for processes with thresholds $E_i \geq 10.2 \text{ eV}$ approximate well to the following analytical form:

$$k_i = k_{0i} \times T_{\text{tail}}^2 \times F(|E|/(N \times a), X_H, T_g) \times \exp(-E_i/T_{\text{tail}}), \quad (1)$$

with $F(|E|/(N \times a), X_H, T_g) = 0.0033 \times u(T_g) \times \exp(150/(|E|/(N \times a))^{0.93})$, where $|E|/(N \times a)$ is in Td, T_g in K, E_i and T_{tail} in eV, and the function $u(T_g) = T_g/2900$ for the $H(n=1) + e$ reactions and $u(T_g) = (T_g/2900) \times (1 + 3.3 \times \exp(-5000/T_g))$ for the $H_2(X) + e$ reactions. T_{tail} is very sensitive to the values of $|E|/(N \times a)$, X_H and T_g and can be approximated as $T_{\text{tail}} = 0.029 \times (|E|/(N \times a))^{0.93} \times (1 + 0.329 \times (X_H - 0.12)) \times (0.959 + 0.9 \times \exp(-8955/T_g))$. The pre-

exponential factors $k\theta_i [\text{cm}^3 \text{eV}^{-2} \text{s}^{-1}]$ are determined by the cross-sections and are presented below.

Maxwell's equations (MEs) for the electric (E_z , E_r) and magnetic (H_ϕ) fields were solved numerically using a finite difference time domain (FDTD) method and treating the electron current density (j) equation and boundary conditions in a manner similar to that outlined by Tan *et al.*³⁷ The coupling between the calculated electric fields and the electron concentration, n_e , is a major challenge when using FDTD methods. A correct description of this coupling requires the self-consistent solution of MEs along with the conservation equations within the 2-D model for charged (and other) species, momentum and energy, with proper accounting for the various interdependences, *i.e.* (n_e , EEDF) $\leftrightarrow |E|/(N \times a)$, absorbed power density $|jE| \leftrightarrow (T_g$ and the neutral species concentrations n_k), (n_e , and the corresponding ion concentrations, n_i) $\leftrightarrow n_k$ (when considering associative ionizations and neutral $\leftrightarrow$ ion inter-conversions), *etc.* In addition, electron-ion recombination processes, ambipolar diffusional transfer of charged species and the loss of such species on the substrate and at the reactor walls should all be accommodated. Such self-consistent 2-D plus ME modelling provides the quasi-steady-state (r , z) distributions of the plasma parameters (species concentrations, EEDF(T_e , T_{tail}), T_g , reaction rates, heat and species fluxes incident on the substrate and on the reactor walls), the substrate (T_{sub}) and quartz window $T_q(r)$ temperatures, and the electromagnetic fields (E_z , E_r , H_ϕ), for any given reactor conditions (p , P , partial and total gas flow rates).

By way of illustration, Figures 9(a) and 9(b) show, respectively, the calculated axial (at $r = 0$) and radial (at $z = 10.5$ mm) distributions of T_g , T_e and T_{tail} (left hand axis) and the average absorbed MW power density $|jE|$, electric $|E|$ and reduced electric $|E|/(N \times a)$ fields (right hand axis) for base conditions. T_e , $|jE|$ and $|E|/(N \times a)$ are all calculated to peak near the substrate (at $z \sim 3$ mm). In contrast to $|jE|$ (and n_e (shown in Figures 10 and 11)), the T_e , $|E|$ and $|E|/(N \times a)$ distributions are each relatively flat throughout the hot plasma core (*i.e.* in the regions $z \sim 8$ – 20 mm (Figure 9(a)) and $r \sim 0$ – 20 mm (Figure 9(b)) with respective values in the ranges of 1.2–1.35 eV, 140–165 V cm⁻¹ and 28–32 Td. Notwithstanding the calculated sharp increase of $|E|$ when approaching the substrate surface, the reduced field $|E|/(N \times a)$ drops at $z < 2.5$ mm as a result of the steeper increase in the gas concentration, $N = p/(kT_g)$, that follows from the decline in $T_g(z)$.

The near constancy of the $|E|/(N \times a)$, $T_e(r, z)$ and $T_{\text{tail}}(r, z)$ values throughout the hot plasma core (Figure 9) does not translate into a corresponding region of near constant electron density, as shown by the axial (at $r = 0$) and radial (at $z = 10.5$ mm) profiles of different species concentrations for base conditions displayed in Figures 10 and 11 respectively. As Figure 10(b) shows, the electron density peaks further from the substrate (at $z \sim 8$ mm), reflecting the efficient diffusional transfer from the maximal net electron source region (at $z \sim 3$ mm) to the substrate and to other cooler regions. Similar arguments apply in the case of the $H(n = 1)$ concentrations. Again, diffusion shifts the peak of the distribution from the region of maximal net production (*i.e.* from $z \sim 11$ mm to $z \sim 15$ mm). Local imbalances in the production and loss rates for the various charged species and for $H(n = 1)$ atoms are compensated by comparable diffusional transfer rates. In contrast, the local production and loss rates of the excited $H(n > 1)$ and H_2^* species are in strong balance, and the concentration profiles shown in Figures 10(a), 10(c), 11(a), and 11(c) are closely related to the spatial profiles of their sources and their quenching rates. Guided by the 2-D modeling, we now analyze the main sources and sinks of the H_2^* and $H(n = 3)$ species studied in the companion experiments, along with other key species (*e.g.* $H(n = 2)$ atoms) that participate in the dominant associative ionization process.

Analogous plots showing the axial (at $r = 0$) and radial (at $z = 10.5$ mm) distributions of T_g , T_e , T_{tail} , $|jE|$, $|E|$ and $|E|/(N \times a)$ calculated for a smaller ($d_{\text{sub}} = 18$ mm) substrate and the same base conditions of p and P are shown in Figure S5, while Figures S6 and S7 show the axial and radial concentration profiles calculated for this smaller substrate for the same species (*i.e.* $H(n = 1, 2, 3)$, electrons, H_3^+ , H_3O^+ , $H_2(X)$ and various H_2^* states) as displayed in Figures 10 and 11. The maximum values of $|jE|$, $|E|$ and $|E|/(N \times a)$ are all higher for $d_{\text{sub}} = 18$ mm (*cf.* $d_{\text{sub}} = 32$ mm) and, as can be seen by comparing Figures 9a and S5a, the maxima of the $|jE|$ and $|E|/(N \times a)$ distributions both shift closer to the substrate upon reducing d_{sub} . These changes are reflected by similar shifts in the column densities of excited species (*cf.* Figures 10 and S6).

3.2.2. The $H(n = 2)$ balance and the main ionization sources.

a) Production reactions: $H(n = 2)$ atoms are mainly formed by electron impact excitation (EIE) of $H(n = 1)$ atoms, for which the threshold energy is $E_2 = 10.2$ eV:

(For this and all other reactions involving collision with electrons readers should recall the relation between the rate coefficients k_i and the pre-exponential factors $k\theta_i$ described in eq. (1)). The rates of radiative cascade from higher levels, $H(n > 2) \rightarrow H(n = 2) + h\nu$, under the conditions of present interest are more than two orders of magnitude lower than the rate of the EIE process (2).

b) Loss reactions: $H(n = 2)$ atoms are subject to strong collisional quenching:⁵⁸

This k_3 value is based on measurements⁵⁸ of the non-radiative quenching (apart from transfer into the $H(2p)$ states) of $H(2s)$ atoms by H_2 molecules, which returned a cross-section $\sigma = 50 \text{ \AA}^2$ for collision velocities in the range $3 \times 10^5 \leq v \leq 10^6 \text{ cm s}^{-1}$. The original study proposed $H_3^+ + e$ as the main products of reaction (3),⁵⁸ but later studies returned a cross section for this proposed associative ionization that was (i) an order of magnitude lower and (ii) showed a much stronger velocity dependence than collisional quenching.⁵⁹ Based on the later measurements,⁵⁹ we have adopted the following temperature-dependent rate coefficient for the associative ionization reaction

The value of k_4 in the plasma core ($k_4 \sim 1.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at $T_g = 3000 \text{ K}$) agrees well with the constant value ($1.66 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) used in our original work³¹ but is two orders of magnitude lower than the value used in ref. 32. The $H(n = 2)$ concentration and thus, via reaction (4), this important contribution to the overall ionization rate is mainly determined by the loss reaction (3) which is assumed to be irreversible and to yield three ground state H atoms. Reaction (4) is the dominant ionization source in the current model throughout the plasma volume at base pressure and above (*i.e.* at $p \geq 150 \text{ Torr}$) but electron impact ionization of H_2 (reaction (5)) gains in relative importance at lower pressures. At $p = 75 \text{ Torr}$, for example, the rate of reaction (5) in the plasma core is predicted to be ~ 2.5 -times greater than that of the associative ionization reaction (4).

The $H(n = 1) + H_2^* \rightarrow H_3^+ + e$ associative ionization reaction is recognized as another potentially important source of ions in the hot plasma region, but a lack of appropriate kinetic data precludes its inclusion in the present modelling. H atom ionization is another important

contributor to the total ionization rate. The rate of electron impact ionization of $H(n = 1)$ atoms

is <25% that of reaction (5) at $p = 75$ Torr, but reaction (6) becomes progressively more important with increasing pressure and its rate is comparable to the H_2 ionization rate (5) at $p \geq 150$ Torr. Under the present plasma conditions, H^+ and H_2^+ ions are rapidly converted to H_3^+ ions via the respective fast reactions $H^+ + 2H_2 \rightarrow H_3^+ + H_2$ and $H_2^+ + H_2 \rightarrow H_3^+ + H$.⁶⁰

The radiative decay $H(2p) \rightarrow H(1s) + h\nu$ (with rate coefficient $A_{2p \rightarrow 1s} = 6.25 \times 10^{-8} \text{ s}^{-1}$) is an important loss mechanism for $H(n = 2)$ atoms in optically thin plasmas, particularly since the $H(2p)$ and $H(2s)$ states are well mixed by collisions with H_2 molecules.⁵⁴ Radiative decay is much less important under the present plasma conditions, however, owing to strong re-absorption on the Lyman- α (and $H(n = 3) \rightarrow H(n = 1)$ Lyman- β) lines. Given an absorption cross-section $\sigma_0 \sim 10^{-13} \text{ cm}^2$ at the line center of the Lyman- α transition,⁶¹ the mean free path for a Lyman- α photon in the hot plasma region under base conditions (where the H atom number density $[H(n = 1)] \sim 5 \times 10^{16} \text{ cm}^{-3}$) will be $\sim 2 \times 10^{-4} \text{ cm}$. Photon re-absorption will be less efficient off line center but, assuming a Voigt profile and a FWHM Doppler width $\Delta\nu \sim 6 \times 10^{11} \text{ s}^{-1}$ appropriate for $T_g \sim 3000 \text{ K}$, we can estimate that the escape factor θ for Lyman- α photons emitted in the plasma core may be as low as 10^{-3} . As a result, the radiative loss process (7),

(with statistical weights $g_{2p} = 6$ and $g_{2s} = 2$) is a much less important loss process for $H(n = 2)$ atoms than the collisional loss processes (3) and (4) under the prevailing plasma conditions. That the employed rate coefficient ($k_3 = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) returns an $H(n = 2)$ column density in the plasma core, $\{H(n = 2)\} \sim 4 \times 10^8 \text{ cm}^{-2}$, in good accord with the value measured in our cavity ring down spectroscopy absorption studies of dilute N_2 in H_2 plasmas operating under very similar process conditions,⁶⁰ provides further (albeit indirect) indication of the necessity of the fast collisional quenching (3).

3.2.3 The $H(n = 3)$ balance.

a) Production reactions: As for $H(n = 2)$, EIE of $H(n = 1)$ atoms is an important source:

In this case, however, near-resonant excitation transfer reactions of the form $\text{H}(n=1) + \text{H}_2^* \leftrightarrow \text{H}(n=3) + \text{H}_2(\text{X})$ involving a limited sub-set of $\text{H}_2^*(v, J)$ excited state molecules^{62,63} could provide another important source of $\text{H}(n=3)$ atoms. This contribution has been included in the current model as reaction (9), using $\text{H}_2(\text{B}^1\Sigma_u^+)$ as a representative H_2^* species⁶² and an effective rate coefficient k_9 :

b) Loss reactions: The $\text{H}(n=3) \leftrightarrow \text{H}_2^*$ coupling reaction also constitutes a significant $\text{H}(n=3)$ atom loss mechanism, which we include in the model by reaction (10):

with, again, $\text{H}_2(\text{B})$ serving as a representative for all near-resonant H_2^* levels. We note, however, that the same result can be obtained by taking $\text{H}_2(\text{a}^3\Sigma_g^+)$ as the representative H_2^* species, with $k_9 = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_{10} = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This smaller k_9 value reflects the larger steady state concentration of $\text{H}_2(\text{a})$ (*cf.* $\text{H}_2(\text{B})$) in the hot plasma region (Figure 11(c)); indirectly, at least, the present calculations hint that the more populated triplet states of H_2 are likely to be the main contributors to the $\text{H}(n=3) \leftrightarrow \text{H}_2^*(v, J)$ excitation transfer. The measured cross-sections for $\text{H}(n=3)$ quenching by H_2 molecules are large ($>75 \text{ \AA}^2$).^{62,63} Lewis and Williams⁶² reported a quenching rate coefficient $k_{10} = 2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (measured at room temperature and derived assuming free escape of Lyman- β emission). This coefficient will be reduced when re-absorption of Lyman- β emission is significant – hence our adoption of a constant value $k_{10} = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in the present modelling.

Such variations in the values of the coefficients k_9 and k_{10} have no significant impact on the relative profiles of $\{\text{H}(n=3)\}(z)$, which is important when comparing with the measured Balmer- α emission intensity profiles, $I_{\text{em}}(\text{H}_\alpha)(z)$. But, without inclusion of processes (9) and (10), we were unable to describe the measured p and P dependences of the Balmer- α emission. The present calculations show that the net loss rate of $\text{H}(n=3)$ atoms via reactions (9) and (10) is comparable to the rate of their production via the EIE reaction (8) throughout the plasma region, under all p and P conditions investigated. The strong $\text{H}(n>2) \leftrightarrow \text{H}_2^*$ coupling invoked here should also reveal itself in other ways. For example, it should affect the quasi-equilibrium between the $\text{H}_2^*(v, J)$ rovibrational populations established via the fast

rovibrational-translational (R-T and V-T) relaxation and vibration-vibration (V-V) exchange processes. Any substantial disturbance of the population distributions within those H_2^* states that emit in the optical range could complicate the determination of rotational and vibrational temperatures from their measured spectra. Further, the proposed $H(n > 2) \leftrightarrow H_2^*$ coupling, together with reactions (2) and (3), would imply that the $H(n \geq 2)$ partitioning cannot be treated simply as a balance of EIE (production) and radiative decay (loss) processes when estimating the electron temperature, T_e .

Other $H(n = 3)$ loss processes include Balmer- α emission (11)

and the associative ionization reactions (12) and (13):

Lacking alternative information, we assume the same values for the rate coefficients k_{12} and k_{13} , while k_{13} was derived from experimental data.⁶⁴ Throughout the entire plasma region, for all p and P conditions investigated, the rates of reactions (11) – (13) were each typically about one order of magnitude lower than the rates of reactions (8) – (10).

3.2.4 The balance of excited state molecular hydrogen, H_2^* .

a) Production reactions: The main source of H_2^* molecules apart from the $H(n > 2) \leftrightarrow H_2^*$ coupling reactions is EIE of ground state $H_2(X)$ molecules. Analysis of published e- H_2 cross-sections⁴⁵⁻⁵³ allows us to elaborate a consistent set of EIE processes for forming the $B^1\Sigma_u^+$, $c^3\Pi_u$, $a^3\Sigma_g^+$, $C^1\Pi_u$ ^{47,49}, $b^3\Sigma_u^+$ ⁵⁰, $e^3\Sigma_u^+$ ⁴⁶ and $d^3\Pi_u$ (ref. 52 and references therein) states of H_2 . The cross-section for excitation to the $d^3\Pi_u$ state was assumed to be the same as for the $e^3\Sigma_u^+$ state, with an appropriate (0.61 eV) shift in the energy scale, while the cross-section for exciting to the $G^1\Sigma_g^+$ state was set equal to that for the $B^1\Sigma_u^+$ state (another $H_2(n = 3)$ singlet state).⁵⁰ Guided by the studies of Liu *et al.*,^{45,48} we have also incorporated an increase of these EIE and ionization cross-sections with increasing T_g which, for the present EEDFs, results in a ~50%-65% increase in the rate coefficients at $T_g = 3000$ K (*cf.* $T_g = 300$ K). These cross-sections, together with the calculated EEDFs, allow derivation of the rate coefficients k_i for EIE from the $H_2(X)$ state approximated by eq. (1) with the $k0_i$ [$\text{cm}^3 \text{ eV}^{-2} \text{ s}^{-1}$] and E_i [eV] values given in Table 1. Indicative k_i values for plasma parameters characteristic of the hot

plasma core (*i.e.* $|E|/(N \times a) = 33.5$ Td, $T_g = 2900$ K, $X_H = 0.12$) are given in the final column of Table 1.

Please insert Table 1 here

EIE into the dissociative $b^3\Sigma_u^+$ state of H_2

constitutes another source of H atoms. The estimated rate coefficient $k_{21} \sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ in the hot plasma region is higher than that of the EIE processes (14) – (20) listed in Table 1, but reaction (21) is only predicted to overtake thermal dissociation of H_2 as the dominant H atom formation mechanism in a thin layer just above the substrate (*e.g.* at $z < 4$ mm under base conditions).

Collisional mixing could be important for near-degenerate states of H_2 , particularly for the metastable $c^3\Pi_u$ and $a^3\Sigma_g^+$ states: $H_2(c) + M \leftrightarrow H_2(a) + M$ with $M = H_2(X)$ or $M = e$.⁶⁵ EIE of these most populated excited states could be potential sources for some of the higher energy radiative states of current interest, but the excitation rate coefficients would need to be unrealistically high ($k \sim 10^{-6} - 10^{-5} \text{ cm}^3 \text{ s}^{-1}$) if such EIE processes were to be competitive with direct EIE from the $H_2(X)$ state. Thus, we have neglected all such excited state EIE processes.

Electron-ion recombination reactions are also not significant contributors to the observed H_2^* emissions. H_2^* formation via the recombination of H_3^+ ions and electrons is at least 2 eV endothermic. The calculated H_2^+ concentration in the hot plasma region is at least 10^5 lower than that of H_3^+ , from which we conclude that the H_2^* yield from electron-ion recombination reactions must be at least 4-orders of magnitude lower than the EIE source.

b) Loss reactions: Radiative decay is included in the current model using detailed data for the radiative transitions (lifetimes) of the following H_2^* states:^{11,66}

The radiative decay rates derived from these rate constants are, respectively, higher (for reaction (26)), comparable to (for reaction (25)) and lower (for reactions (22-24)) than the corresponding rates of collisional quenching on $\text{H}_2(\text{X})$ molecules under the conditions of present interest. Large quenching cross-sections have been reported from room temperature measurements⁵⁸ and used in MW PACVD models,^{25,26} but their temperature dependence (*e.g.* their values at $T_g \sim 3000$ K) is not known. Further, careful inspection of the available data for the quenching of $\text{H}_2(\text{G})$ molecules on $\text{H}_2(\text{X})$ (fig. 7 in ref. 62 returns significantly smaller values for the cross-section ($\sim 13 \text{ \AA}^2$) and quenching rate coefficient ($\sim 2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) than those presented in Table 1 of ref. 62 ($100 \text{ \AA}^2$ and $9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively). As a first approach, we have assumed the corrected quenching coefficient for all H_2^* excited states included in the model, *i.e.*:

Trial variations of this rate coefficient over a wide range ($5 \times 10^{-11} \leq k_{27} \leq 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) result in predictable (inversely proportional) changes in the absolute H_2^* concentrations but only minor changes to their relative spatial profiles. Moreover, any substantial change to the chosen value for k_{27} leads to a poorer correlation between the calculated pressure dependences of the $\{\text{H}_2(\text{e})\}$, $\{\text{H}_2(\text{d})\}$, $\{\text{H}_2(\text{G})\}$ and $\{\text{H}(n = 3)\}$ column densities and the respective measured $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ emission intensities.

3.3 Comparing model outputs with experiment

The H and H_2 plasma kinetics described in sections 3.2.2 – 3.2.4 and the 2-D self-consistent model developed in section 3.2.1 were used to simulate the various P and p regimes explored experimentally. Figures 12(a) and 12(b) compare the calculated z -dependent column densities and measured emission intensities (I_{em}) of, respectively, $\text{H}_2(\text{e}, v = 0)$ molecules and $\text{H}(n = 3)$ atoms for $P = 0.7, 1.5$ and 1.85 kW, with $p = 150$ Torr and $d_{\text{sub}} = 32$ mm. The calculations succeed in reproducing the P -dependent variations in the relative magnitudes of both $I_{\text{em}}(\text{H}_2^*(\text{e-a}))$ and $I_{\text{em}}(\text{H}_\alpha)$, and the shift (to smaller z) of the $I_{\text{em}}(\text{H}_2^*(\text{e-a}))$ distribution with increasing P . The modelling also predicts a similar shift in the peak of the $I_{\text{em}}(\text{H}_\alpha)$ distribution – a trend that is only hinted at by the experimental data (see Figure 12(b)). Both the plasma volume, V_p (which we define as the volume in which the absorbed power density $|jE|$ is $>10\%$ of the maximal $|jE|$ value), and the volume of the plasma emission, V_{em} (defined

as the volume in which the H_2^* emission rates are $>10\%$ of the maximal emission rate), increase with power – mainly in the radial direction. V_{em} is typically $\sim 25\%$ smaller than V_p , and both V_{em} and V_p show $\sim P$ dependences. The maximum T_g and n_e values are calculated to increase by 6% and 40% , respectively, upon increasing P from 0.7 to 1.5 kW and both start to saturate at higher input powers. This increase in T_g drives a ~ 3 -fold increase in the maximal $X(\text{H})$ value. The maximum T_e and T_{tail} values barely change across this range of input powers, but their axial profiles are much flatter at low P (0.7 kW). As Figure 9(a) showed, the peaks of the T_e , T_{tail} and $|jE|$ profiles are all predicted to shift closer to the substrate with increasing P (e.g. from $z \sim 6$ mm at $P = 0.7$ kW to $z \sim 3$ mm at $P \geq 1.5$ kW).

The self-consistent 2-D model calculations succeed in reproducing the observed P -dependent trends in $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ well, and serve to highlight the myriad factors (changes in the effective plasma volume, the electron density and electron characteristics and, in the case of the H atoms, T_g and the degree of dissociation) that may contribute to an observed change in emission intensity.

Figures 13(a) and 13(b) compare the calculated $\{\text{H}_2(\text{e}, v=0)\}(z)$ and $\{\text{H}(n=3)\}(z)$ column densities and the measured $I_{\text{em}}(\text{H}_2^*(\text{e-a}))$ and $I_{\text{em}}(\text{H}_\alpha)$ profiles at $p = 75, 150$ and 250 Torr (and constant $P = 1.5$ kW). Similar comparisons for the $\text{H}_2(\text{d})$ and $\text{H}_2(\text{G})$ states are shown in Figure S8 in the Supplementary Information. Again, the 2-D modelling broadly reproduces the experimental emission profiles and their non-trivial scaling with p , but fails to capture details of the measured profiles at small z (most evidently at low p). The contrasting decrease in $I_{\text{em}}(\text{H}_2^*(\text{e-a}))$ and increase in $I_{\text{em}}(\text{H}_\alpha)$ with increasing p are explained by the respective changes in V_p and the plasma parameters: $|E|/(N \times a)$, T_e and T_{tail} all decrease with p (e.g. by $\sim 15\%$ upon increasing p from 75 to 250 Torr), while the maximum T_g , X_{H} and n_e values all increase as p is raised from 75 to 250 Torr. The respective deviations in these latter quantities (relative to $p = 150$ Torr) are $\sim \pm 3.5\%$ in T_g and $\sim \pm 65\%$ in both X_{H} and n_e . V_p and V_{em} both show an approximate $1/p$ decrease (in both the radial and axial directions). The present calculations confirm the main effects of varying p and P revealed and described in the earlier studies (that did not involve direct calculation of the electromagnetic fields)^{60,67} but also show that the maximal electron concentration scales with pressure ($n_e \sim p$) – mainly as a result of the strong increase in the associative ionization rate. The new self-consistent modelling also returns a more radially confined plasma and thus higher (and maybe slightly overestimated) maximal values of n_e , T_g and X_{H} . The striking decrease in $\{\text{H}_2^*\}$ with

increasing p – notwithstanding the parallel increase in n_e – is induced by the decline in T_{tail} and the increase in the quencher ($\text{H}_2(\text{X})$) concentrations. These same trends and effects must apply also for $\text{H}(n = 3)$, but these are more than counter-balanced by another positive effect of increasing p – the substantial increase in the $\text{H}(n = 1)$ concentration, which boosts $\text{H}(n = 3)$ production by both EIE (eq. 8) and by the excitation transfer reaction (eq. 9).

The substrate temperature distribution $T_{\text{sub}}(r, z)$ assumed in the model is determined from the heat flux on the substrate (from thermal conduction in the gas and from adsorption and recombination of H atoms⁶⁸) and analytical solution of the thermal conduction equations in the substrate and in the gas gap between the substrate and water cooled base of the reactor. Similar procedures were used to estimate the temperature distribution in the quartz window $T_{\text{q}}(r, z)$. We note that the calculated T_{sub} values show minimal radial variation and that the values ($T_{\text{sub}} = 600, 800$ and 970 K for $p = 75, 150, 250$ Torr, respectively, at $P = 1.5$ kW, and $T_{\text{sub}} = 600$ and 900 K for $P = 0.7$ and 1.85 kW, respectively, at $p = 150$ Torr, all for $d_{\text{sub}} = 32$ mm) are systematically lower than the T_{sub} values measured by pyrometry. This is not expected to introduce any substantial inconsistencies, as running the current 2-D model with the experimentally derived T_{sub} values has only a modest effect on the calculated H_2^* and $\text{H}(n = 2, 3)$ column densities in the near substrate region and negligible impact once more than a few mm from the substrate surface. Estimations of the blackbody emission from the substrate and infrared (IR) plasma emission reflected from the substrate show that the latter, in particular, could perturb pyrometer measurements of not just H_2 plasmas but also $\text{H}_2/\text{rare gas}$ and $\text{H}_2/\text{C}_x\text{H}_y$ plasmas. For smaller substrate diameters (*e.g.* $d_{\text{sub}} = 18$ mm), the 2-D model predicts an increase in T_s – as observed experimentally – but only to ~ 1100 K (*cf.* 800 K for $d_{\text{sub}} = 18$ mm) under base p and P conditions) and that the maximal $\{\text{H}_2^*\}$ shifts nearer to the substrate (peaking at $z = 1.5$ mm). As Figure S9 (Supplementary Information) shows, the predicted absolute increase in the maximal $\{\text{H}_2^*\}$ is only about half that observed experimentally (Figure 6a), though the predicted absolute increase in the $\{\text{H}(n = 3)\}$ values is more consistent with the experimental results (Figure 6b).

As the comparisons in Figures 12 and 13 show, the present calculations do not fully reproduce the observed trends at small z . Several possible reasons for these discrepancies have been considered. One contributory factor is likely to be the neglect of non-local effects like diffusive transfer of electron energy and electron conduction in the modelling. Ionization and electron-ion (*i.e.* $e + \text{H}_3^+$ and $e + \text{H}_3\text{O}^+$) recombination are not in local balance in all p

and P regimes modelled, and any net ionization is accommodated by the diffusional transfer of charged species to the substrate, to the reactor base and to the cooler off-plasma regions. As the insets in Figures 7, S3 and S4 show, the plasma emission is visibly brighter at the substrate edge, plausibly the result of local maxima in the EM field that are not properly captured in the self-consistent modelling, but which may contribute significantly to $I_{\text{em}}(\text{H}_2^*)$ and $I_{\text{em}}(\text{H}_\alpha)$ intensities measured at $z \sim 0$. We have also investigated one other substrate-related effect – possible photoinduced emission of electrons from the substrate by incident vacuum ultraviolet radiation from the H_2 plasma (*e.g.* by H atom Lyman series emissions or $\text{H}_2^*(\text{B-X})$ Lyman or (in part) (a–b) continuum emissions (eqs. (26) and (25), respectively). Any photoelectrons arising from photons emitted in process (26), for example, would be ejected with initial energies ~ 7 eV and gain energy in the thin, near substrate sheath region where the typical voltage drop may be as much as $\sim 15\text{--}25$ V. The relaxation of these electrons has been investigated using Monte Carlo methods,⁶⁹ leading to the conclusion that $\sim 55\%$ of the energy associated with these photoelectrons is likely to be expended in H_2 dissociation (reaction (21)) in the near substrate region, that only $\sim 8\%$ of the energy induces additional ionization, and that such photoelectrons have relatively little impact on the calculated H atom, ion/electron, and H_2^* densities and distributions predicted by the reported 2-D modelling.

4 Conclusions

This combined experimental and modelling study offers new insights into a topic of longstanding fundamental interest: a hydrogen plasma. The plasma under investigation is MW-activated and operates under conditions relevant to contemporary diamond CVD reactors, *i.e.* at a high gas temperature ($T_g \sim 3000$ K) and moderate pressure ($p \sim 150$ Torr). These plasmas are non-thermal ($T_e \gg T_g$) and only weakly ionized (degree of ionization $\alpha \sim 10^{-6}$ in the core region).³¹

The experiment returns spatially resolved optical emission spectra from the d, G and e excited states of H_2 and from the $\text{H}(n=3)$ level, as functions of three variables: pressure, p , applied MW power, P , and substrate diameter, d_{sub} . The experimental data are compared and contrasted with the outputs of a self-consistent 2-D (r, z) model of the plasma-chemical, transport and electromagnetic processes. Such comparisons allow us to characterize the dominant plasma (and plasma emission) generation mechanisms prevailing in such MW-

activated H_2 plasmas, to reveal hitherto unrecognised contributions from associative ionization processes and to illustrate how spatially resolved H_2^* (and $H(n = 3)$) emission measurements can provide a sensitive probe of the hyperthermal component of the EEDF. Specifically, the combination of experiment and self-consistent modelling shows that the EEDF in the plasma volume is a very sensitive function of the reduced electric field, the atomic hydrogen mole fraction and the gas temperature. Reliable modeling of the plasma requires a proper description of the EEDFs and the various electron production/loss and diffusive transfer processes, all of which are strongly coupled with the (spatially dependent) MW electromagnetic fields and power absorption. Further, important coupling reactions between hydrogen atoms and molecules are identified, including the quenching of $H(n > 2)$ atoms by H_2 and of H_2^* molecules by $H(n = 1)$ atoms and the associative ionization reaction (4) (the rate of which is T_g dependent), all of which need to be recognized in order to reproduce the measured spatial profiles of the H_2^* and H_α emissions and their non-trivial dependences on p and P .

Associated content

The following Supporting Information is available free of charge on the ACS Publications website at DOI: ???????????????????.

$I_{em}(\lambda, z)$ images in the wavelength ranges 423-497 nm and 563-636 nm from a MW activated hydrogen plasma operating under base conditions: $p = 150$ Torr, $P = 1.5$ kW, $F(H_2) = 300$ sccm, $d_{sub} = 32$ mm and $d_{wire} = 0.01$ ". Each image is accompanied by a $I_{em}(\lambda)$ plot of the summed intensities (in the height range $3 \leq z \leq 6$ mm), highlighting lines in each spectrum that were used in preparing the $I_{em}(H_2^*, G-B)$ and $I_{em}(H_2^*, d-a)$ vs z plots shown in Figure 3. Spatial profiles of (a) $I_{em}(H_2^*)$ obtained by analysing regions of d-a emission and (b) $I_{em}(H_\alpha)$ for a MW activated hydrogen plasma operating at three pressures ($p = 75, 150$ and 275 Torr) with $d_{sub} = 17$ mm, $d_{wire} = 0.004$ " and $P =$ (i) 0.9 and (ii) 1.85 kW.

Axial (at $r = 0$) and radial (at $z = 10.5$ mm) distributions of T_g , T_e , T_{tail} , $|jE|$, $|E|$ and $|E|/(N \times a)$, and $H(n = 1, 2, 3)$, electrons, H_3^+ , H_3O^+ , $H_2(X)$ and various H_2^* states) concentration profiles calculated for a smaller ($d_{sub} = 18$ mm) substrate and base conditions of p and P .

Comparisons of calculated column densities and measured emission intensities of $H_2(G, v = 0)$ and $H_2(d, v = 0)$ molecules for $p = 75, 150$ and 250 Torr, with $P = 1.5$ kW and $d_{sub} = 32$ mm.

Comparisons of calculated column densities and measured emission intensities of (a) $\text{H}_2(\text{d}, \nu=0)$ molecules and (b) $\text{H}(n = 3)$ atoms for two substrate diameters ($d_{\text{sub}} = 17$ mm (experiment) / 18 mm (modelled), and 32 mm) with, in both cases, $p = 150$ Torr, $P = 1.5$ kW and $d_{\text{wire}} = 0.01''$.

Author Information

Corresponding Authors

*E-mail: mike.ashfold@bristol.ac.uk; ymankelevich@mics.msu.su

Notes

The authors declare no competing financial interests.

All underlying experimental data are available at the University of Bristol data repository, data.bris, at <https://doi.org/10.5523/bris.2spimvgp4waj629g6zt6v6qil9>.

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Table 1

Rate Coefficients k_i for EIE from the $H_2(X)$ State Approximated by eq. (1) with the Specified k_0 and E_i Values and the Following Characteristic Plasma Parameters: $|E|/(N \times a) = 33.5$ Td, $T_g = 2900$ K, $X_H = 0.12$.

Reaction	H ₂ Excited State Populated by EIE	$k_0 / \text{cm}^3 \text{eV}^{-2} \text{s}^{-1}$	E_i / eV	$k_i / \text{cm}^3 \text{s}^{-1}$
(14)	B ¹ Σ _u ⁺	$k_{014} = 7.74 \times 10^{-7}$	$E_{14} = 11.30$	$k_{14} = 1.56 \times 10^{-13}$
(15)	c ³ Π _u	$k_{015} = 1.91 \times 10^{-6}$	$E_{15} = 11.75$	$k_{15} = 2.13 \times 10^{-13}$
(16)	a ³ Σ _g ⁺	$k_{016} = 3.18 \times 10^{-6}$	$E_{16} = 11.79$	$k_{16} = 3.36 \times 10^{-13}$
(17)	C ¹ Π _u	$k_{017} = 5.15 \times 10^{-7}$	$E_{17} = 12.40$	$k_{17} = 2.44 \times 10^{-14}$
(18)	e ³ Σ _u ⁺	$k_{018} = 1.95 \times 10^{-7}$	$E_{18} = 13.36$	$k_{18} = 2.61 \times 10^{-15}$
(19)	d ³ Π _u	$k_{019} = 3.51 \times 10^{-7}$	$E_{19} = 13.97$	$k_{19} = 2.10 \times 10^{-15}$
(20)	G ¹ Σ _g ⁺	$k_{020} = 1.52 \times 10^{-7}$	$E_{20} = 13.99$	$k_{20} = 8.89 \times 10^{-16}$

Figure 1

Selected singlet and triplet states of H_2 , the ground state of the H_2^+ ion, and states of atomic H, referenced to a common zero of energy. To reference the molecular states correlating with any given $\text{H}(n=1) + \text{H}(n>1)$ dissociation limit, the atomic energy levels would need to be raised by the bond dissociation energy, $D_0(\text{H}-\text{H}) = 4.48 \text{ eV}$. Transitions monitored by OES in the present study are highlighted.

Figure 2

(a) $I_{em}(\lambda, z)$ image (where $z = 0$ defines the substrate surface) in the wavelength range 825-895 nm from a hydrogen plasma operating under base conditions: $p = 150$ Torr, $P = 1.5$ kW, $F(H_2) = 300$ sccm, $d_{sub} = 32$ mm and $d_{wire} = 0.01$ ". (b) $I_{em}(\lambda)$ plot of the summed emission intensities in the range $3 \leq z \leq 6$ mm over the wavelength range $850 \leq \lambda \leq 870$ nm, with R branch lines of the e-a (0,0) band identified.

Figure 3

Spatial profiles of $I_{\text{em}}(\text{H}_2^*)$ e-a, d-a and G-B emissions and $I_{\text{em}}(\text{H}_\alpha)$ emission from a MW activated hydrogen plasma operating under base conditions. The various distributions have been normalised to the same peak intensity and plotted using the same pen color as used to indicate the emission in Figure 1.

Figure 4

Spatial profiles of (a) $I_{\text{em}}(\text{H}_2^*, \text{e-a})$ emission, (b) $I_{\text{em}}(\text{H}_\alpha)$ emission and (c) the summed intensities of $I_{\text{em}}(\text{H}_2^*)$ (red) and $I_{\text{em}}(\text{H}_\alpha)$ (black) emissions in the ranges $z = 2.25 \pm 0.75$ mm and $z = 8.25 \pm 0.75$ mm (open and filled symbols, respectively) for a MW activated hydrogen plasma operating at a range of input powers, P , with all other parameters held at their base values. The relative intensities in (a) and (b) are displayed on a common vertical scale. The dashed lines in (c) illustrate the linear P dependences of both emissions at low z .

Figure 5

Spatial profiles of (a) $I_{\text{em}}(\text{H}_2^*, \text{e-a})$ emission, (b) $I_{\text{em}}(\text{H}_\alpha)$ emission and (c) the summed intensities of $I_{\text{em}}(\text{H}_2^*)$ (red) and $I_{\text{em}}(\text{H}_\alpha)$ (black) emissions in the ranges $z = 2.25 \pm 0.75$ mm and $z = 8.25 \pm 0.75$ mm (open and filled symbols, respectively) for a MW activated hydrogen plasma operating at a range of pressures, p , with all other parameters held at their base values. The relative intensities in (a) and (b) are displayed on a common vertical scale. Dashed lines in (c) illustrate the $\sim p^{-1}$ dependence of the $I_{\text{em}}(\text{H}_2^*, \text{e-a})$ emission at low z once p exceeds ~ 100 Torr.

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Figure 6

Spatial profiles of (a) $I_{\text{em}}(\text{H}_2^*, \text{d-a})$ emission and (b) $I_{\text{em}}(\text{H}_\alpha)$ emission for a MW activated hydrogen plasma operating with three different substrate diameters, d_{sub} , with all other parameters held at their base values. The relative intensities in any given plot are displayed on a common vertical scale. The measured T_{sub} values were 690 °C, 920 °C and 1315 °C for $d_{\text{sub}} = 32, 27$ and 17 mm, respectively.

Figure 7

Spatial profiles of (a) $I_{\text{em}}(\text{H}_2^*, \text{d-a})$ and (b) $I_{\text{em}}(\text{H}_\alpha)$ emissions for a MW activated hydrogen plasma operating at three pressures with a substrate diameter $d_{\text{sub}} = 17 \text{ mm}$, $d_{\text{wire}} = 0.004''$ and $P = 1.5 \text{ kW}$. The relative intensities in any given plot are displayed on a common vertical scale. The inset in (b) shows tilt view images of the plasma above the substrate (indicated by the ellipse extending beyond the $p = 150 \text{ Torr}$ image), apertured by the slot shaped viewing port. The measured T_{sub} values are, respectively, below the detection limit, 910°C and 940°C for $p = 75 \text{ Torr}$ (red), 150 Torr (black) and 275 Torr (blue).

Figure 8

Normalized EEDFs ($f(\epsilon)/\int f(\epsilon)d\epsilon$, shown on a logarithmic scale) for various combinations of reduced electric field, $|E|/(N \times a)$, gas temperature, T_g , and H atom mole fraction, X_H , with the following T_e and T_{tail} values (in eV): $T_e = 1.39$, $T_{tail} = 0.76$ (for $|E|/(N \times a) = 33.5$ Td, $T_g = 2900$ K, $X_H = 0.12$), $T_e = 1.16$, $T_{tail} = 0.64$ (27 Td, 3200 K, 0.18), $T_e = 1.06$, $T_{tail} = 0.61$ (26.5 Td, 2900 K, 0.12), $T_e = 0.94$, $T_{tail} = 0.59$ (27.3 Td, 1653 K, 0.04), $T_e = 0.78$, $T_{tail} = 0.46$ (19.6 Td, 2900 K, 0.12).

Figure 9

Calculated (a) axial (z , $r = 0$) and (b) radial ($z = 10.5$ mm, r) distributions of T_g , T_e and T_{tail} (left hand axis) and the average absorbed MW power density $|jE|$, and electric $|E|$ and reduced electric $|E|/(N \times a)$ fields (right hand axis) for base conditions.

Figure 10

Calculated axial (z , $r = 0$) concentration distributions of (a) $H(n = 1, 2, 3)$ atoms, (b) the dominant charged species and (c) the ground and selected excited states of H_2 for base conditions. Note that the distributions in (a) and (c) are plotted on a logarithmic scale.

Figure 11

Calculated radial ($z = 10.5$ mm, r) concentration distributions of (a) $H(n = 1, 2, 3)$ atoms, (b) the dominant charged species and (c) the ground and selected excited states of H_2 for base conditions. Note that the distributions in (a) and (c) are plotted on a logarithmic scale.

Figure 12

Comparisons of the calculated column densities (symbols, defined in Inset in (a)) and measured emission intensities (lines, defined in inset in (b)) of (a) $\text{H}_2(\text{e}, v=0)$ molecules and (b) $\text{H}(n=3)$ atoms for $P = 0.7$ kW (red), 1.5 kW (black) and 1.85 kW (purple), with $p = 150$ Torr and $d_{\text{sub}} = 32$ mm.

Figure 13

Comparisons of the calculated column densities (symbols, defined in inset in (a)) and measured emission intensities lines, defined in inset in (b)) of (a) $\text{H}_2(\text{e}, v = 0)$ molecules and (b) $\text{H}(n = 3)$ atoms for $p = 75$ Torr (red), 150 Torr (black) and 250 Torr (blue), with $P = 1.5$ kW and $d_{\text{sub}} = 32$ mm.

TOC Graphic

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TOC graphic

67x42mm (300 x 300 DPI)

Figure 1

82x85mm (300 x 300 DPI)

Figure 2

82x129mm (300 x 300 DPI)

Figure 3

82x60mm (300 x 300 DPI)

Figure 4

82x171mm (300 x 300 DPI)

Figure 5

82x171mm (300 x 300 DPI)

Figure 6

82x119mm (300 x 300 DPI)

Figure 7

82x119mm (300 x 300 DPI)

Figure 8
82x60mm (300 x 300 DPI)

Figure 9

82x119mm (300 x 300 DPI)

Figure 10

82x165mm (300 x 300 DPI)

Figure 11

82x165mm (300 x 300 DPI)

Figure 12

82x109mm (300 x 300 DPI)

Figure 13

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