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Evidence of catalytic production of hot hydrogen in RF generated hydrogen/argon plasmas

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Abstract

This is the third in a series of papers by our team on apparently anomalous Balmer series line broadening in hydrogen containing RF generated, low-pressure (< 600 mTorr) plasmas. In this paper the selective broadening of the atomic hydrogen lines in pure H_2 and Ar/H_2 mixtures in a large general electronics conference (GEC)-type cell (36 cm length × 14 cm ID) was mapped as a function of position, H_2/Ar ratio, time, power, and pressure. Several observations regarding the selective line broadening were particularly notable as they are unanticipated on the basis of earlier models. First, the anomalous broadening of the Balmer lines was found to exist throughout the plasma, and not just in the region between the electrodes. Second, the broadening was consistently a complex function of the operating parameters, particularly gas composition (highest in pure H_2) position, power, and pressure. Clearly, not anticipated by earlier models were the findings that under some conditions the highest concentration of "hot" (> 10 eV) hydrogen was found at the gas entry end, and not in the high-field region between the electrodes, and that in other conditions, the hottest H was at the (exit) pump (also grounded electrode) end. Third, excitation and electron temperatures (measured optically) were less than 1 eV in all regions of the plasma not directly adjacent (> 1 mm) to the electrodes, providing additional evidence that the energy for broadening, contrary to standard models, is not obtained from the electric field. Fourth, in contrast to our earlier studies of hydrogen/helium and water plasmas, we found that in some conditions 98% of the atomic hydrogen was in the "hot" state throughout the GEC-type cell. Virtually every operating parameter studied impacted the character of the hot H atom population. Clearly, second and third order effects exist, indicating a need for experimental design. Some non-field mechanisms for generating hot hydrogen atoms are outlined.

Keywords: Balmer series; Line broadening; RF plasma; Classical quantum mechanics; Argon; Hydrogen; GEC cell

1. Introduction

For more than 15 years there have been reports of selective broadening of the Balmer series α line in low-pressure (ca. < 100 Pa) pure hydrogen, radio frequency (RF) and DC generated H_2/Ar plasmas [1–10]. New reports continue to appear [11], including several reports that selective H_α line broadening is found in other plasmas including H_2/He in a radio frequency general electronics conference (RF-GEC)-type cell [12], water vapor (both in microwave [13] and RF-GEC-type cell [14]), and hydrogen gas in the presence of certain catalysts including helium, argon, potassium, and strontium in glow discharge, RF-GEC-type, and filament-type cells [15–22]. In all prior cases, other than those described in Refs. [12–22], the selective broadening was studied exclusively for hydrogen and H_2/Ar plasmas and with one exception [23] exclusively in high-field regions between the electrodes. Also, with one notable exception [24] no other studies outside of our group have employed microwave systems.

In all previous reports it is noted the broadening was limited to hydrogen atoms (e.g. no broadening of Ar ion or hydrogen molecule lines), and there is universal agreement regarding the origin of the broadening, namely it is due to a Doppler shift. Generally, there is agreement that the energy of the "hot" hydrogen between the electrodes is greater than 20 eV.

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With the exception of our team, there is universal agreement about the mechanism of energy input to the hydrogen. Specifically, apart from very recent changes (see Discussion section) proposed by one team [23], and our own consistent support for the classical quantum mechanics (CQM) model, there has been universal support in the literature for a "field acceleration" origin of the observed hot hydrogen. It should be noted, as discussed later in detail, that there are several variations of the field effect model, each with some differences in the details of the mechanism of selective energy transfer to the atomic H.

The present work was inspired by the unusual nature of the observed phenomenon, and uncertainty regarding the ability of all the field acceleration models to explain already published phenomena. In particular, it is not clear that the "field acceleration" class of models can explain: (i) a bimodal (or trimodal) distribution of neutral (i.e. H atom) temperatures, (ii) neutral species temperatures more than 30 times higher than those of electrons in a RF plasma, (iii) symmetric Doppler broadening even in the absence of reflecting surfaces, and (iv) recent, but limited, indications that the angle of observation relative to the direction of the electric fields has no impact on the characteristics of the broadened line. Regarding the second point: nowhere else in the literature of plasma physics is there a mechanism postulated that creates a body of neutral species hotter than any of the charged species. Certainly nowhere else is there a mechanism postulated for generating neutral species that are far hotter than electrons in any type of plasma. Regarding the third and fourth points: recent experimental results in the literature suggests symmetric line broadening even in the absence of reflecting surfaces appears to contradict the predictions of the field acceleration models as a class.

The method of testing the field acceleration class of models required an experimental design both more thorough and more comprehensive than prior studies of Balmer series line broadening in low-pressure (between approximately 15 and 90 Pa) RF generated H_2/Ar plasmas. For example, the field acceleration models all require a high field to selectively produce high-energy atomic hydrogen. Thus, the experiments conducted in this study were designed to search for Balmer series line broadening well outside the high-field regions. Also, the field acceleration model predicts that the observed line broadening should be impacted by the angle of orientation relative to the accelerating field. According to all variations of the field effect modes, observation perpendicular to the field should show little broadening and that parallel to the field should show a preferential red or blue shift as a function of alignment relative to the cathode/anode. Thus, the experiment was designed to permit observation parallel and perpendicular to the principle field directions. It must also be noted that although the experiments were primarily designed to test field acceleration models, the alternative model of selective line broadening, based on CQM theory, is inevitably "tested" by novel data. Thus, the scientific standing of the CQM model, in view of both earlier data and the data collected in this report, is also discussed.

2. Experimental

2.1. Plasma hardware

As described in earlier reports, all plasmas were generated in a GEC-type cell [15,16], through which gas mixtures flow, held at pressure between 15 and 90 Pa. This system consists of a large cylindrical (14 cm ID × 36 cm length) Pyrex chamber with two steel circular (8.25 cm diameter) plates, placed about 1 cm apart at the center (Fig. 1). An RF generator at 13.6 MHz (RF VII, Inc., Model RF 5) was used to couple power to the plates using an impedance matching network.

A hollow stainless steel tube (ID 0.95 cm) supplied power to the powered electrode plate. The hollow tube was sealed to the electrode plate with a small (approx. 1 cm diameter) quartz window. The tube itself was vacuum sealed to the chamber with Ultratorr fittings clamped to its outside at the end of the vacuum chamber. Thus, the hollow center was open from the laboratory to the window at the center of the electrode. This arrangement facilitated the end-on observation of the plasma between the electrodes in the direction parallel to the electric field by allowing the light fiber to be brought directly to the electrode center, pointing parallel to the field direction. All parts, chamber, power supply, gauges, spectrometer, etc., were grounded with a heavy-duty aluminum foil, as this was found to dramatically improve the signal-to-noise ratio. Gases, UHP grade (99.999%) Ar, H_2, and Xe, were metered into the chamber through Ultratorr fittings at one end, about 18 cm from the electrodes, using independent mass flow controllers (MKS) for each gas. To test for the purity of the H_2 only plasmas, efforts were made to find the Ar line at 696 nm, a line readily found in the mixed gas plasmas. Absolutely no argon signal at this wavelength was detected in the pure hydrogen plasmas.

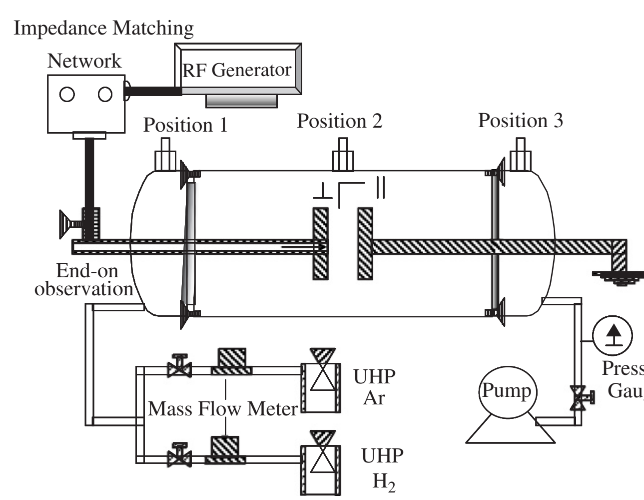

Fig. 1. Schematic of the quartz GEC-type system. Note that the cell is 14 cm in diameter and 36 cm in length. The cell itself was placed in a grounded blackened aluminum lined box and the fiber optic probe was surrounded by a sheath of grounded aluminum foil as well. Grounded shielding reduced noise significantly. A 1 cm quartz window in the powered electrode allows end-on observation of Position 2 parallel (Position 2P) to the electric field.