Publ. Astron. Obs. Belgrade No. 102 (2022), 247 - 250 *Contributed Paper*

SPECTROSCOPIC DETERMINATION OF THE DEGREE OF DISSOCIATION OF HYDROGEN IN THE GLOW DISCHARGE

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Abstract. The optical emission spectroscopy technique is used to measure the degree of dissociation of hydrogen along the axis of cylindrical abnormal glow discharge parallel (side-on) to the copper cathode surface in hydrogen - argon mixture at low pressure. The degree of dissociation is determined from the intensity ratio of the H_γ line and the diagonal Fulcher-α bands, while the electric field strength distribution in the cathode sheath region is determined from the measured Stark shifts of the experimental profiles of the hydrogen Balmer gamma line H_γ.

1. INTRODUCTION

Within a growing number of applications, Glow Discharge Sources (GDS) are successfully used as excitation sources for analytical spectroscopy of metal and alloy samples, see e.g. Jakubowski et al. 2003 and Broekaert 2003. Most GDS applications are based on the original design described by Grimm 1968, with both direct current (DC) and radio frequency (RF) excitations.

The knowledge of discharge parameters, like the degree of dissociation of molecular hydrogen in hydrogen and hydrogen-containing low-temperature plasmas, is of common interest in basic research, industrial applications, and understanding the outer space phenomena, see Lavrov et al. 2006.

In this study, the optical emission spectroscopy (OES) technique is used to estimate the degree of dissociation of a hydrogen-argon mixture in a low-pressure Grimm-type glow discharge. For this purpose, the hydrogen H_γ line and emission spectra of the $d^3\Pi^-_u \rightarrow a^3\Sigma^+_g$ system are recorded and analysed in the cathode sheath region of the discharge.

2. EXPERIMENTAL

A detailed description of a modified Grimm GDS is given in Majstorović et al. 2013 and thus, only a few important details will be mentioned here. The experiment was realized in a hydrogen-argon (5% vol. Ar) mixture; further details can be found in Vasiljević et al. 2020.

The axial intensity distribution of radiation has been observed side-on through the anode slot, see Figure 1. The discharge tube was translated in approximately 0.25 mm steps. The light from the discharge was focused with an achromatic lens (focal length 75.8 mm) with unity magnification onto a 20 μm entrance slit (height restriction 2 mm) of 2 m focal length Ebert type spectrometer with 651 g/mm reflection grating blazed at 1050 nm. For the line shape measurements, the reciprocal dispersion of 0.37 nm/mm is used throughout this experiment. All spectral measurements were performed with an instrumental profile very close to Gaussian form with measured full width at half maximum (FWHM) of 8.2 pm.

Thermoelectrically cooled Hamamatsu CCD (2048 × 506 pixels, pixel size 12 × 12 μm, -10 ºC) was used as a radiation detector, and the collected data were transferred to and processed by a PC.

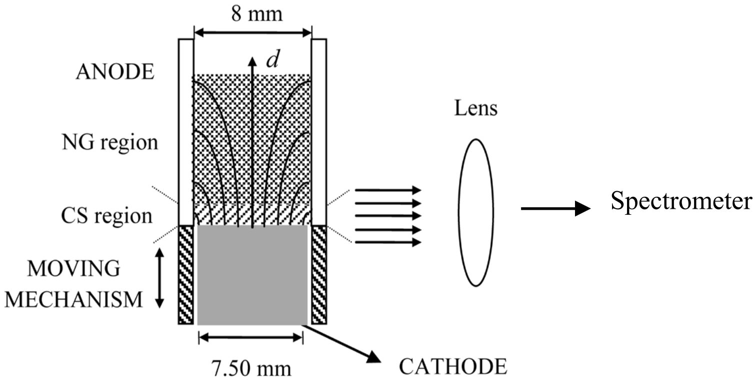

Figure 1: Schematic diagram of the central part of the Grimm GD for side-on observations. Symbols: CS – cathode sheath region, NG – negative glow region.

3. RESULTS AND DISCUSSION

Some recent studies, e.g., Fantz et al. 2006 and Dang et al. 2016, suggest that the ratio of the intensity of the hydrogen Balmer gamma line and Fulcher-α system is a proper value for estimation of the degree of dissociation of hydrogen. It is well known that the atomic hydrogen density is correlated with the Balmer line emission, while the molecular density is correlated with the emission of molecular radiation (Fulcher-α band transition: $d^3\Pi^-_u \rightarrow a^3\Sigma^+_g$, $v' = v'' = 0$–3, $\lambda = 590$–645 nm). The ratio of the emission rate coefficients for H_γ and H_2 is found almost independent of the electron temperature T_e and barely dependent on electron density n_e if 5×10^{16} m^{-3} $< n_e <$ 5×10^{18} m^{-3}, see e.g. Fantz et al 2006 and references therein. Thus, the intensity ratio, H_γ /H_2, is considered suitable for the determination of the density ratio [H] / [H_2] in our GDS as well.

In Figure 2 we present recorded rotational bands belonging to the H_2 Fulcher-α diagonal bands. From the recorded spectra, it is evident that the lines of P, Q and R branch in the visible 590-645 nm wavelength region (wavelength data taken from Crosswhite 1972), are well resolved and have a high signal to noise ratio. In this study we used the intensities of all lines of the electronic transition $d^3\Pi^-_u, v' \rightarrow a^3\Sigma^+_g, v''$ ($v'=v''=0,1, 2, 3$), see Vasiljević et al. 2020.

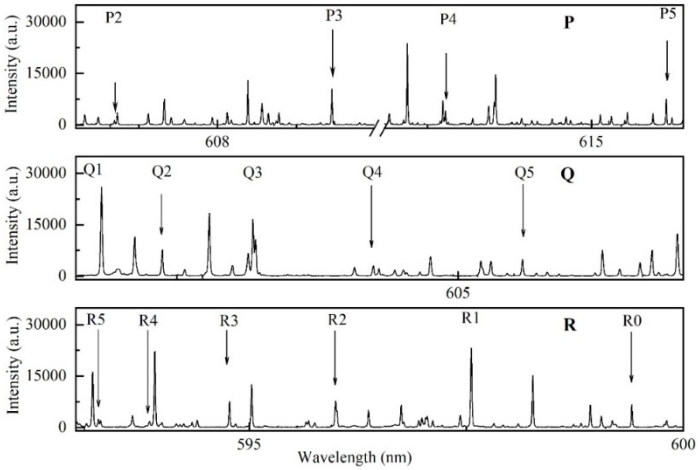

Figure 2: Emission spectra of the rotational lines for the $d^3\Pi^-_u, v'=0 \rightarrow a^3\Sigma^+_g, v''=0$ band, P, Q and R-branches, recorded in the second order of diffraction grating. Experimental conditions: cooper cathode GDS in H_2+5%Ar at p = 4.5 mbar; I = 13.4 mA; U = 646 V.

The intensity ratio, according to Fantz et al. 2006 and Dang et al. 2016 is:

$$\frac{I_\gamma}{I_{Ful.}} = \frac{X_\gamma^{eff}}{X_{H_2.}^{eff}} \frac{[\mathrm{H}]}{[\mathrm{H_2}]}, \qquad (1)$$

where $[\mathrm{H}]$ and $[\mathrm{H_2}]$ are the number densities of hydrogen atoms and molecules and $\frac{X_\gamma^{eff}}{X_{H_2}^{eff}}$ is the ratio between the effective emission rate for the H_γ line and Fulcher-α system molecular radiation calculated according to the collisional radiative model (Fantz et al. 2006). Owing to the high resolution spectrometer, we were able to determine the intensity of the Fulcher-α band. The value for $\frac{X_\gamma^{eff}}{X_{H_2}^{eff}}$ was taken from Figure 5 in Fantz et al. 2006, and the ratio $\frac{I_\gamma}{I_{H_2}}$ was calculated to determine $\frac{[\mathrm{H}]}{[\mathrm{H_2}]}$. Using the relationship between the neutral particle density ratio and the degree of dissociation from Lavrov et al. 2006 and Dang et al. 2016 we estimated the degree of dissociation expressed as:

$$\mathrm{D} = \frac{[H]}{[H] + 2[H_2]} = \frac{\frac{[H]}{[H_2]}}{\frac{[H]}{[H_2]} + 2}. \qquad (2)$$

The electric field strength measurement is performed using the value of the Stark shift coefficient s for the chosen Stark component, and its Stark shift $\Delta\lambda = \Delta\lambda_{p\text{-}p}/2$; here, $\Delta\lambda_{p\text{-}p}$ is peak-to-peak distance, measured on the recorded line shape between the two strongest Stark components that are equally shifted, one to the red, and the other to the blue wavelength side. The so-obtained electric field distributions were fitted using the linear regression and the results suggest that the thickness of the CS region is around 1.75 mm, which is in good agreement with the result obtained using the H_α line published in Vasiljević et al 2020.

Presented results show that the degree of dissociation doesn't vary a lot through the CS region and decreases around the edge with the negative glow region. The thickness of the CS region is used when showing the changes in the intensity and degree of dissociation in Figure 3.

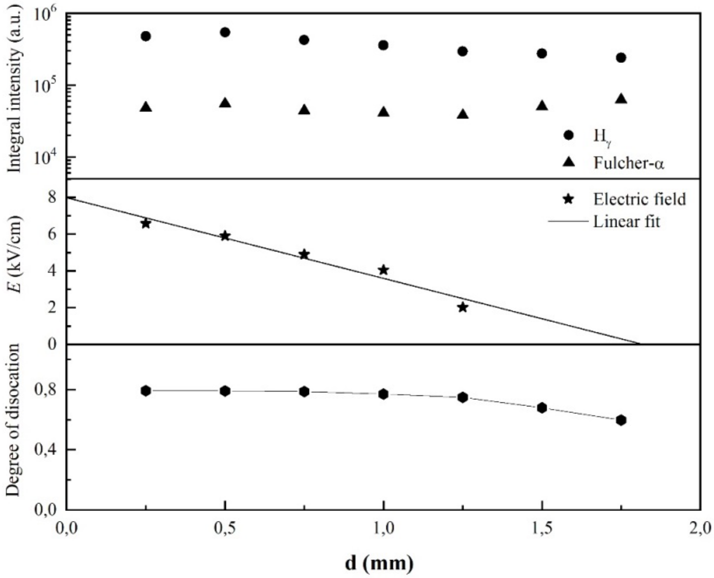

Figure 3: The dependence of: (a) Relative intensity of H_γ line and Fulcher-α bands ($v'=v''=$ 0, 1, 2, 3) (b) Electric field strength and (c) Degree of dissociation, all upon the distance from the cathode. Experimental conditions: cooper cathode Grim GD in H_2+5%Ar at p = 4.5 mbar; I = 13.4 mA; U = 646 V.

Acknowledgments

This work is supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

References

Broekaert J. A. C. : 2003, *Glow Discharge Plasmas in Analytical Spectroscopy*, Marcus R. K. and Broekaert J. A. C., New York: Wiley.

Dang J. J., Chung K-J., Hwang Y. S. : 2016, *Rev. Sci. Instrum.*, **87**, 053503.

Fantz U., Falter H., Franzen P., Wunderlich D., Berger M., Lorenz A., Kraus W., McNeely P., Riedl R., Speth E. : 2006, *Nucl. Fusion*, **46**, S297.

Grimm W. : 1968, *Spectrochim. Acta B*, **23,** 443.

Jakubowski N., Bogaerts A. and Hoffmann V. : 2003, *Atomic Spectroscopy in Elemental Analysis*, Sheffield: Cullen M, Blackwell Publishing.

Lavrov B. P., Pipa A. V. and Röpcke J. : 2006, *Plasma Sources Sci. Technol.*, **15**, 135.

Majstorović G. Lj., Ivanović N. V., Šišović N. M., Djurović S., Konjević N. : 2013, *Plasma Sources Sci. Technol.*, **22**, 045015.

Vasiljević M. M., Majstorović G. Lj., Spasojević D., Konjević N. : 2020, *J. Quant. Spectrosc. Radiat. Transfer*, **254**, 107195.