doi:10.14311/ppt.2018.3.122
Plasma Physics and Technology **5**(3):122–124, 2018

GAS TEMPERATURE DISTRIBUTION OF HYDROGEN IN CATHODE FALL REGION OF GRIMM GLOW DISCHARGE

G. Majstorović[a,*], M. Vasiljević[b], N. Šišović[b]

[a] *Military Academy, University of Defence, Pavla Jurišića Šturma 33, 11105 Belgrade, Serbia*
[b] *Faculty of Physics, University of Belgrade, P.O. Box 44, 11001 Belgrade, Serbia*
[*] gordana.majstorovic@va.mod.gov.rs

Abstract. Optical emission spectroscopy technique was used to measure gas temperature along the axis of cylindrical abnormal glow discharge parallel to the copper cathode surface (side-on) in hydrogen-argon mixture at low pressure. The rotational temperature of excited state of H_2 was determined from the rotational structure of Q branch of Fulcher-α diagonal bands using Boltzmann plot technique while the obtained ground vibrational state temperature is assumed to be equal to gas temperature. The temperature T_0 determined from the rotational population density distribution in an excited vibrational state can be considered as a valid estimation of the ground state temperatutre i.e. H_2 gas temperature.

Keywords: spectroscopy, hydrogen molecule, rotational temperature measurement.

1. Introduction

Within the growing number of applications glow discharge sources (GDS) are successfully used as an excitation source for analytical spectroscopy of metal and alloy samples [1, 2]. The most of GDS applications are based on original Grimm design [3, 4] with direct current (DC) or radio frequency (RF) excitation. The knowledge of discharge parameters, like the electric field strength distribution and gas temperature of molecules in cathode fall (CF) region, is of particular importance for characterization of Grimm GDS. To measure gas temperature Fulcher-α diagonal bands are recorded and analyzed in the cathode fall region of the Grimm type glow discharge operating in an hydrogen – argon mixture at low pressure by means of optical emission spectroscopy (OES). Stark polarization spectroscopy of hydrogen Balmer alpha and beta lines is used for electric field strenght mapping and boundary estimation between the CF and the negative glow (NG) region.

2. Experimental

A detailed description of a modified Grimm GDS is given in [4, 5], thus only few important details will be mentioned here. The experiments were realized in an hydrogen-argon (5% vol. Ar) mixture. The continuous flow of about 300 cm^3/min of gas was sustained at room temperature in the pressure range 2-10 mbar by means of needle valve and two two-stage mechanical vacuum pumps. The reported results for gas pressure represent an average between gas inlet and outlet pressure measurements. To run the discharge, a current stabilized power supply (0-2 kV, 0-100 mA) was used. A ballast resistor of 5.3 kΩ was placed in series with the discharge and the power supply.
The axial distribution of intensity of radiation has been observed side-on through the anode slot, i.e. normal to the direction of electric field vector. The discharge tube was translated along the axis in approximately 0.25 mm steps. For the H_α and H_β experiments the radiation from discharge was polarized by a plastic polarizer. Selection of the π - polarized profile was experimentally carried out by orienting the polarizer axis parallel to the discharge axis, whereas the $d^3\Pi_u^-, \nu' \rightarrow a^3\Sigma_g^+, \nu''(\nu' = \nu'' = 0, 1, 2)$ band lines were observed without the polarizer.

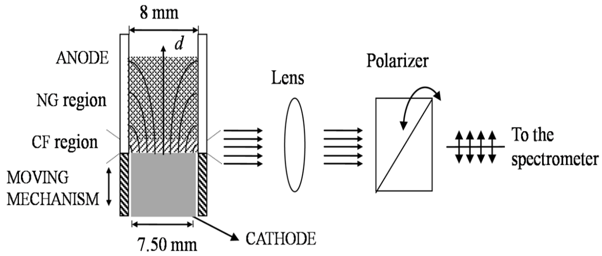

Figure 1. Schematic diagram of the central part of the Grimm GDS and the experimental setup.

The light from the discharge was focused with an achromatic lens (focal length 75.8 mm) with 1:1 magnification onto the 20 μm entrance slot (height restriction 2 mm) of a 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. Measured full width at half maximum (FWHM) of the instrumental profile was 8.2 pm, with the profile very close to the Gaussian of that FWHM.

3. Results and discussion

The temperature obtained from Q branch of Fulcher-α band may be considered as the most reliable for the temperature estimation, see e.g. [6]. Now, we investigate the possibility of using Q branches of the $d^3\Pi_u^-$ $\nu' = 0,1,2 \rightarrow a^3\Sigma_g{}^+$, $\nu'' = 0,1,2$ molecular system for temperature measurement in hydrogen-argon mixture Grimm GDS. The electric field strength distribution in the CF region of the Grimm type GDS is determined by means of the peak-to-peak technique applied to the π-polarized profiles of the first two lines of the hydrogen Balmer series, see Figure 4 in [7]. Here one should note that the same technique, applied to the σ-polarized and unpolarized profiles, essentially gives the same results, as is shown in [5] in the case of π- and σ-polarized profiles.

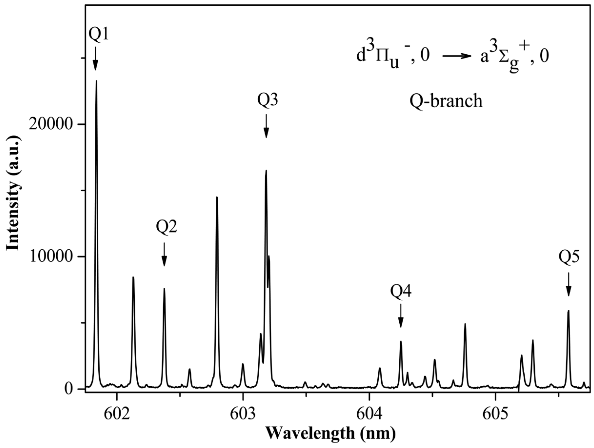

Figure 2. Emission spectra of rotational lines for $d^3\Pi_u^-, \nu \rightarrow a^3\Sigma_g{}^+$ system; Q-branch (with $\nu' = \nu'' = 0$) recorded in the second order of diffraction grating. Experimental conditions: copper cathode Grimm GDS in $H_2 + 5\% Ar$ at $p = 4.5 mbar$; $I = 12 mA$; $U = 775 V$.

From the recorded spectra, see Figure 2, it was evident that Q branch lines of the electronic transition $d^3\Pi_u^-$, $\nu' \rightarrow a^3\Sigma_g{}^+$, $\nu''(\nu' = \nu'' = 0,1,2)$ are well resolved and have high enough intensities in the 595-645 nm wavelength region (wavelength data are taken from [8]). The recorded rotational bands of the ($d^3\Pi_u^- \rightarrow a^3\Sigma_g{}^+$) hydrogen transition are used for evaluation of rotational temperature T_{rot} (n', ν') of excited state using Boltzmann plot technique.
The logarithm intensity of a spectral line of rovibronic transition $(n', \nu', N' \rightarrow n'', \nu'', N'')$ is a linear function of the upper level energy. By plotting $\ln\left(\frac{I^{n',\nu',N'}_{n'',\nu'',N''}}{\nu^4 g_{a.s} H_{N',N''}}\right)$; (ν is a wave number, $g_{a.s}$ - the statistical weight of the n', ν', N' rovibronic level, caused by nuclear spin and the symmetry with respect to the permutation of the nuclei ('a' or 's'), $H_{N',N''}$- Hönl-London (HL) factors [9, 10]) against term values for upper level a straight line is obtained, whose slope $\frac{hc}{kT_{rot}(n',\nu')}$ may be used for determination of the rotational temperature $T_{rot}(n', \nu')$ of excited state, see Figure 3a. In low pressure discharges, due to small collision frequencies, lower than the radiative decay

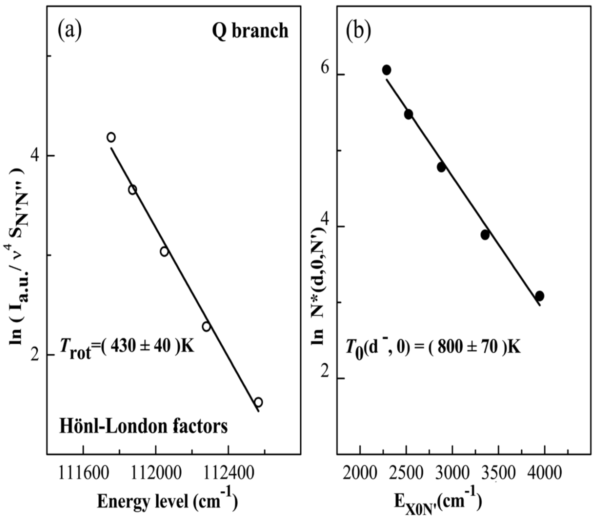

Figure 3. Semi logarithmic plot of population densities for rovibronic levels of H_2 calculated from measured intensities with: (a) Hönl-London factors and (b) Semilogarithmic plot of rotational population densities of $d^3\Pi_u^-$ versus rotational energy of the molecular hydrogen ground state ($X^1\Sigma_g^+(\nu = 0)$). Experimental conditions: same as in Figure 2.

frequencies of the excited state, the number of collisions is not sufficient to redistribute the rotational population. The lifetime values for ro-vibrational levels of electronic state $d^3\Pi_u^-$ [9] of the H_2 molecule, short to allow thermal equilibrium with the working gas, have been used to calculate radiative decay of this state which is $\sim 2.5 \cdot 10^7 s^{-1}$. Under our experimental conditions, neglecting the collision quenching, the collision frequency [11] is not larger than the radiative decay of this state and the number of collisions is not sufficient to redistribute the rotational population. The larger pressure would provide collision frequency larger than the radiative decay and the neutral species rotational collision mixing during the lifetime of the $d^3\Pi_u^-$ state would be sufficient to ensure equilibrium of the rotational distribution of this state with the gas temperature. Within the framework of model discussed in [9], the rotational temperature of ground vibrational state $T_0(n', \nu')$, determined from the rotational population density distribution in an excited (n', ν') vibrational state can be considered as a valid estimation of the ground state rotational temperature, i.e. H_2 gas temperature.
Thus, values of the rotational temperature derived from the population of Q branch vibrational states $\nu' = 0,1,2$ were recalculated to determine T_0 of the ground vibronic state $X^1\Sigma_g^+(\nu = 0)$ at different position, see Figure 3b and the upper part of Figure 4. The results obtained for rotational temperature distribution along the CF region, presented in Figure 4 show that both temperatures, T_0 and T_{rot} (Q branch; $\nu' = 0,1,2$), change along cathode fall region

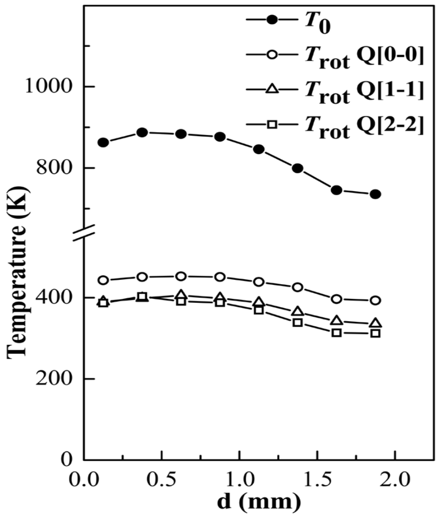

Figure 4. The dependence the rotational temperature of the excited state $d^3\Pi_u^-$ *measured from Q-branch* $\nu' = \nu'' = 0, 1, 2$ *of the Fulcher-*α *band system and the rotational temperature* T_0 *recalculated from the population of Q branch* ν' *= 0,1,2 (estimated error is 7%) for the ground vibronic state* $X^1\Sigma_g^+(\nu = 0)$ *upon distance from cathode. Temperature* T_0 *of the* $X^1\Sigma_g^+(\nu = 0)$ *corresponds to gas temperature while the thickness of CF is less than* 1.375 *mm. Experimental conditions: same as in Figure 2.*

Grimm GDS.The boundary between the CF and the NG region determined by means of electric field measurement. For the electric field measurement in the cathode fall region, Stark polarization spectroscopy of hydrogen Balmer alpha and beta lines is employed and estimated the thickness of CF, see Figure 4 in [7]. In our case, the temperature recalculated for the ground vibrational state $X^1\Sigma_g^+(\nu = 0)$, see [6], is two times larger than the rotational temperature of excited states since the rotational constants [12] for the upper $d^3\Pi_u^-$ and ground $X^1\Sigma_g^+$ $(\nu = 0)$ states are (30.364 cm^{-1}) and (60.853 cm^{-1}), respectively.

4. Conclusion

The discharge observations were carried out parallel to the cathode surface i.e. side-on to the discharge axis. The axial distribution of rotational temperature of the excited state $d^3\Pi_u^-$ in cathode fall region of the Grimm GDS along the direction perpendicular to the cathode surface d is determined using Boltzmann plot technique. The values of the rotational temperature derived from the population of Q branch vibrational states $\nu' = 0, 1, 2$ were recalculated using (2) in [6] to determine T_0 of the ground vibronic state $X^1\Sigma_g^+(\nu = 0)$, which is assumed to be equal to gas temperature.

Acknowledgements

This work is supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia under Project 171014.

References

[1] N. Jakubowski, A. Bogaerts and V. Hoffmann Atomic Spectroscopy in Elemental Analysis, (Sheffield: Cullen M., Blackwell Publishing) Glow discharges in emission and mass spectrometry, 2003

[2] J. A. C. Broekaert Glow Discharge Plasmas in Analytical Spectroscopy, p. 28, (eds. R. K. Marcus and J. A. C. Broekaert, New York: Wiley), 2003

[3] W. Grimm Spectrochim. Acta B, 23(443), 1968 doi: 10.1016/0584-8547(68)80023-0

[4] G. Lj. Majstorović, N. V. Ivanović, N. M. Šišović, S. Djurović and N. Konjević Plasma Sources Sci. Technol., 22:045015, 2013 doi: 10.1088/0963-0252/22/4/045015

[5] Dj. Spasojević, V. Steflekova, N. M. Šišović and N. Konjević Plasma Sources Sci. Technol., 21:025006, 2012 doi: 10.1088/0963-0252/21/2/025006

[6] G. Lj. Majstorović, N. M. Šišović, N. Konjević Plasma Sources Sci Technol., 16:750, 2007 doi: 10.1088/0963-0252/16/4/009

[7] M. M. Vasiljević, G. Lj. Majstorović, Dj. Spasojević and N. M. Šišović, 21th Simposium on Application of Plasma Processes (Štrpske Pleso, Slovakia), SAPP XXI Book of Contributed Papers 213, 2017.

[8] H. M. Crosswhite, The hydrogen molecule wavelength tables (Gerhard Heinrich Dieke, New York: Wiley-Interscience), 1972

[9] S. A. Astashkevich, M. Käning, E. Käning, N. V. Kokina, B. P. Lavrov, A. Ohl and J. Röpcke, JQSRT 56:725, 1996, doi: 10.1016/S0022-4073(96)00103-3

[10] I. Kovacs, Rotational Structure in the Spectra of Diatomic Molecules (London: Adam Hilger LTD) pp. 131, 1969.

[11] L. Tomasini, A. Rousseau, G. Gousset, and P. Leprince, J. Phys. D: Appl. Phys. 29:1006, 1996 doi: 10.1088/0022-3727/29/4/010

[12] G. Herzberg, Molecular spectra and molecular structure vol I, p. 125, (New York: Van Nostrand-Reinhold), 1950.