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EUROFUSION CP(15)01

Many authors

20th Symposium on Application of Plasma Processes

(17th January – 22nd January 2015)
Tatranska Lomnica, Slovakia

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

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ROTATIONAL TEMPERATURES IN HYDROGEN AND HYDROGEN-ARGON DC DISCHARGE

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Ro-vibrational emission spectrum of Lyman system was simulated and studied. Rotational temperatures of Fulcher-αsystem, Lyman system of hydrogen and of the second positive system of nitrogen were compared. Gas temperature was 440K. Influence of heavy collisions on rotational temperature of hydrogen emission systems was considered at pressures 80 and 400 Pa. Changes of emission spectra with amount of argon in the discharge were observed because of resonance reactions with resonant state of argon.

1. Introduction

Discharges in hydrogen have wide applications in chemical vapour deposition growth of graphene [1, 2], diamonds [3], in formation thin layers [4] and many others. For all applications, diagnostics of plasma is very important and gas temperature is one of the most important parameter of plasma. Problem of hydrogen plasma is non-thermalized molecular states at low pressures [5] and difficulties with determination of gas temperatures from hydrogen emission spectra. We have studied emission spectra of Lyman system and Fulcher-α system and the second positive system of nitrogen. Gas temperature was determined from emission spectra of the second positive system and compared with Lyman and Fulcher-α system. Influence Ar on experimental spectra was observed.

2. Experimental set-up

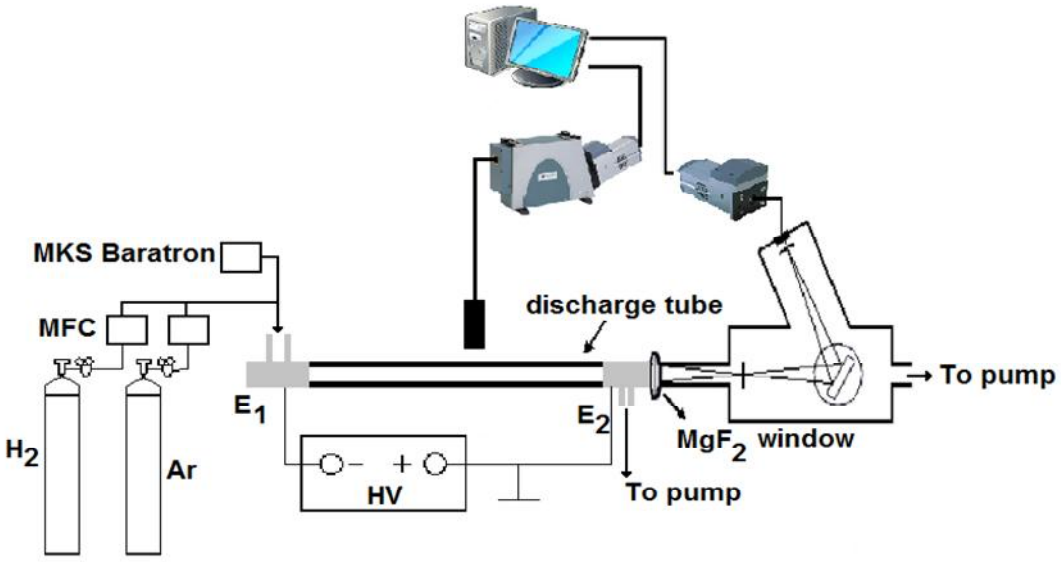

Fig. 1.: Experimental set-up. MFC – mass flow controller, E_1, E_2 – electrodes, MKS Baratron – pressure gauge.

The experimental set-up including the spectroscopic devices is shown in figure 1. The flowing plasma is sustained in a Simax tube (18mm inner diameter, 26 cm length). The discharge is ignited in H_2 and H_2–Ar mixtures (purity grades of 99.9990% and 99.996% for hydrogen and argon,

respectively). The gas is evacuated by an oil rotary pump. The total gas pressure is measured by a capacitive gauge MKS Baratron controlled by a throttle valve. The flow rates are controlled by mass-flow MKS and AERO controllers. The total flow rate is fixed to 22 sccm for gas pressure of 400 Pa and 4.4sccm for gas pressure of 80 Pa. The distance between the electrodes is 26 cm. Electrodes are made from brass and they are used also as vacuum exchange labels. The discharge pulse is maintained by a DC voltage source providing up to -2 kV, 30 mA (ISEG). We have studied the hydrogen–argon plasma at 10 mA with different percentages of argon ranging from 0 to 90 in the mixture. The optical signal is collected by a quartz optical fibre placed perpendicular to discharge in the middle of tube. The collected signal is recorded with an Andor Mechelle-5000 spectrometer coupled with an Andor iStar intensified camera in the wavelength range 200–950 nm. Resolution of Mechelle spectrometer is $\lambda/\Delta\lambda = 4000$. The integral light emitted from the discharge in the axial direction came through MgF_2 window and the input slit of a VUV spectrometer. The MgF_2 window served for separation of discharge tube and VUV spectrometer (McPherson) with Andor iStar intensified camera. Instrumental function of VUV spectrometer has Gaussian profile with FWHM of 0.18 nm and wavelength range 115-300 nm.

3. Results and discussion

3.1 Rotational temperature of H_2 ($d^3\Pi^-_u$)

Rotational temperature of $H_2(d^3\Pi_u^-)$ is determined from Boltzmann distribution of rotational transitions of the vibrational (v'- v'' = 2-2, 1-1) of Fulcher-α band of Q-branch. Other branches, P and R are perturbed by higher Σ states [6].Intensities of 5 rotational lines were fitted by Gaussian profile. Intensity of rotational line can be written as

$$I \sim (2\Gamma_N + 1) S^{dN'}_{aN''} exp\left(\frac{-B_v N'(N'+1)hc}{kT_{rot}}\right) \quad (1)$$

Rotational constant is $B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right)$ and $B_e = 30.364$ cm^{-1}, $\alpha_e = 1.545$ cm^{-1}[7] for $H_2(d^3\Pi_u^-)$state. It is taken in account total nuclear spin due to presence orto- ($\Gamma_{N'} = 1$) and para-states ($\Gamma_{N'} = 0$) of H_2. $\Gamma_{N'} = 1$ for N' even and $\Gamma_{N'} = 0$ for N' odd, respectively. $S^{dN'}_{aN''} = \frac{2N'+1}{2}$is Hönl-London factor, T_{rot} is rotational temperature of the state.

3.2 Rotational temperature of N_2 ($C^3\Pi_u$)

Low amount of impurities allows us to determine rotational temperature of $N_2(C^3\Pi_u)$ state. Rotational temperature is determined by the best fit of synthetic and experimental spectra of the transition $N_2(C^3\Pi_u, v' = 0 \rightarrow B^3\Pi_g, v'' = 2)$ and $N_2(C^3\Pi_u, v' = 1 \rightarrow B^3\Pi_g, v'' = 3)$ using Specair program [8]. The typical accuracy is ±50 K.

3.3 Simulation of Lyman system of H_2 ($B^1\Sigma^+_u$)

The theoretical construction of the H_2 spectra is based on the conventional description of the diatomic molecules spectra analysis, which can be found e. g. in [7, 9]. For intensity of rotational line can be written:

$$I^{v'J'}_{v''J''}(\lambda_i) \sim \frac{hc}{\lambda^{v'J'}_{v''J''}} A^{v'}_{v''} \frac{S^{J'}_{J''}(\Gamma_{J'}+1)}{\sum_{J'} exp\left(\frac{-F_{v'}(J')hc}{kT_{rot}}\right) \sum_{v'} exp\left(exp\left(\frac{-G_{v'}hc}{kT_{vib}}\right)\right)} \times$$

$$\times \exp\left(\frac{-F_{v'}(J')hc}{kT_{rot}} - \frac{G_{v'}hc}{kT_{vib}} - \frac{1}{2}\left(\frac{\lambda_i - \lambda^{v'J'}_{v''J''}}{\sigma}\right)^2\right) \quad (2)$$

Lyman system consists from 2 branches, P (ΔJ= -1) and R (ΔJ = +1).We did not find this kind of simulation in any papers. But we could find several sets of different equilibrium constants available. To avoid of possible imprecise constants, we tried to use always experimental data for simulation as much as it was possible. Positions of rotational lines were taken from Abril et al. [10]. Wavelength of rotational lines is proportional to difference of energies upper and lower state. By suitable difference of two wavelengths is possible to determine requested energies $F_{v'}(J')$ and $G_{v'}$. $FWHM = \sigma\sqrt{8ln2}$ and Höln-London factors were calculated according formula (3)

$$S \sim \frac{A(2J'+1)\lambda^3}{band\ strength} \qquad (3)$$

Where A is Einstein coefficients and band strengths were taken from [11]. There is comparison of simulation and experimental spectra in fig.2.

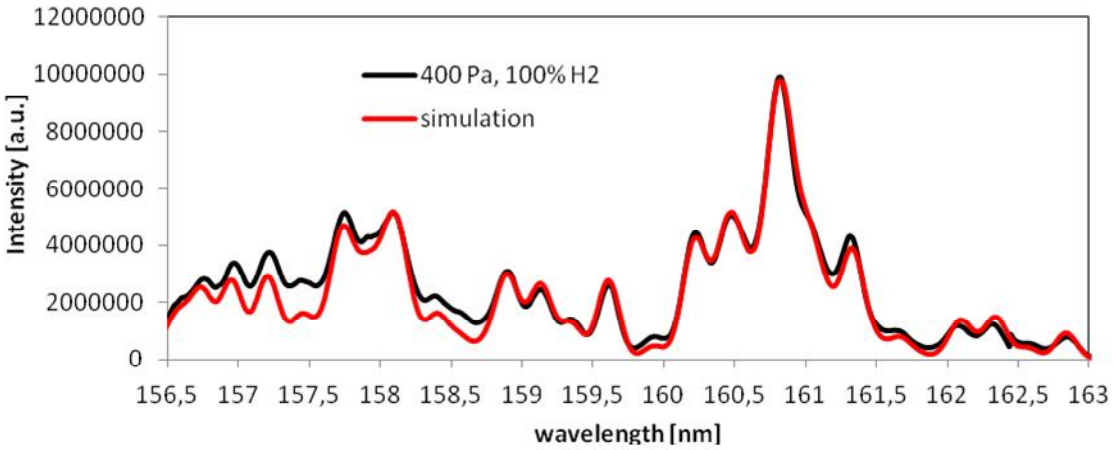

Fig. 2.: Comparison of experimental spectra (black) and simulation (red) of Lyman system.

3.4 Gas temperature

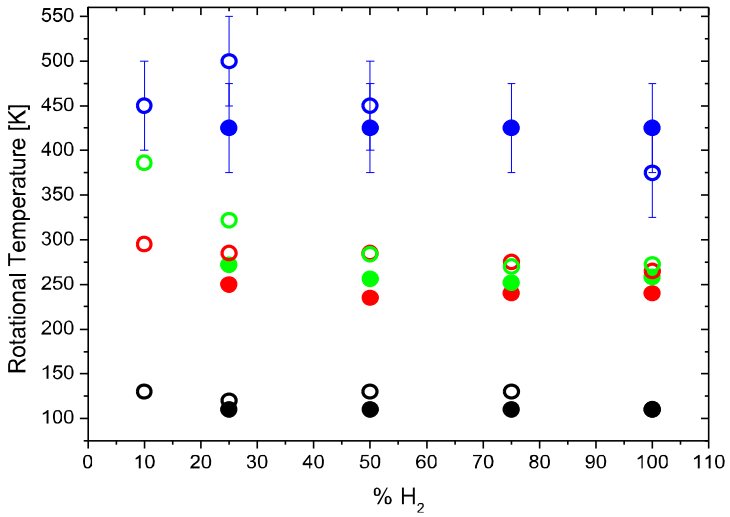

Fig. 3: Rotational temperatures at 80 Pa (full circles) and 400 Pa (empty circles) of $N_2(C^3\Pi_u)$ (blue), $H_2(B^1\Sigma^+_u)$ (black), $H_2(d^3\Pi^-_u,v'=1)$ (green), $H_2(d^3\Pi^-_u,v'=2)$ (red).

Rotational temperatures of $N_2(C^3\Pi_u)$ state at 80 Pa and 400 Pa are close to each other. Average value is 440 K for all measured concentration of H_2. This value is assimilated with gas temperature. Rotational temperatures of $H_2(d^3\Pi^-_u,v'=1)$ and $H_2(d^3\Pi^-_u,v'=2)$ are also close to each other and equal to 250 K at 80 Pa and 290 K at 400 Pa and of $H_2(B^1\Sigma^+_u)$ equal to 110 K at 80 Pa and 130 at 400 Pa. Molecular hydrogen states are not thermalized because of short time of life but rotational distribution of$H_2(d^3\mathbf{\Pi}_u^-)$ states are very often used for determination of gas temperature if rotational levels are populated mainly by electrons with Maxwell distribution. It is supposed that the rotational distribution of $H_2(d^3\mathbf{\Pi}_u^-)$ copies rotational distribution of ground state $H_2(X^1\Sigma_g^+)$. Then it is assumed that rotational distribution of ground state $H_2(X^1\Sigma_g^+)$ is in equilibrium with gas temperature. Difference between both rotational energies ($H_2(X^1\Sigma_g^+)$ and $H_2(d^3\mathbf{\Pi}_u^-)$) lies in rotational constant. So

$$T_{rot}(H_2(X^1\Sigma_g^+)) = (B_{vg}/B_v)\times T_{rot}(H_2(d^3\mathbf{\Pi}_u^-)) = T_g. \quad (4)$$

Ratio of B_{vg}/B_v depends on vibration level of upper state and it is equal to 2.24 for $H_2(d^3\Pi^-_u, v'=2)$ state and equal to 2.11 for $H_2(d^3\Pi^-_u, v'=1)$. If this procedure is used at our conditions we would get 100-200 K higher gas temperature depending on pressure. Real ratio of $T_g/T_{rot}(H_2(d^3\mathbf{\Pi}_u^-))$ = 1.7 at 80 Pa and 1.5 at 400 Pa. Ratio 1.7 was measured at 133 Pa by Tomasini et al. [12].

Emission spectrum of Lyman system consists from many overlapping vibrational bands and our resolution of spectrometer is not sufficiently low to resolve them. Technique of ratio of B_{vg}/B_v is probably not possible to use but further research have to be done, we observed ratio $T_g/T_{rot}(H_2(B^1\Sigma^+_u))$ 3.9 (80 Pa) and 3.4 (400 Pa).

Difference can be caused by lower values of rotational constants of upper state of Lyman transitions.

3.5 Relative density of H_2 ($B^1\Sigma^+_u$, v = 3)

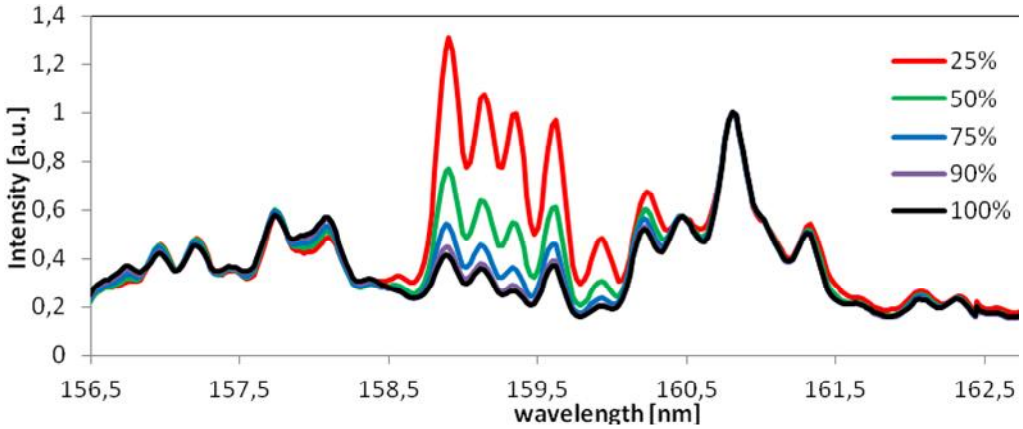

Fig. 4.: Emission spectra of $H_2(B^1\Sigma^+_u)$ in the mixture H_2-Ar in dependence of concentration of H_2.

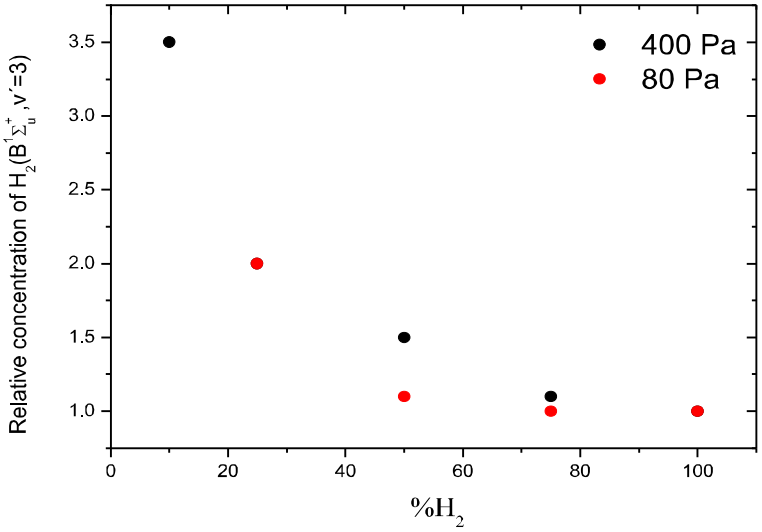

Fig. 5.: Evolution of concentration of $H_2(B^1\Sigma^+_u, v'=3)$ in the mixture H_2-Ar in dependence of concentration of H_2.

Argon has no influence on rotational temperature in studied range of Lyman system (156.5 – 163) nm. We observed increasing intensity of transition $H_2(B^1\Sigma^+_u, v'=3 \rightarrow X^1\Sigma^+_g, v=10)$. This behaviour can be explained by resonance reaction of H_2 $(B^1\Sigma^+_u, v'=3)$ states with resonant states of argon Ar($^3P_1$, $^1P_1$) [13]:

a) $H_2(X^1\Sigma^+_g, v=0, J) + Ar(^3P_1) \rightarrow H_2(B^1\Sigma^+_u, v'=3, J') + Ar$ (5)

b) $H_2(X^1\Sigma^+_g, v=0, J) + Ar(^1P_1) \rightarrow H_2(B^1\Sigma^+_u, v'=3 \text{ and } 4, J') + Ar$ (6)

Relative density of $H_2(B^1\Sigma^+_u, v'=3)$ (normalized to density in pure hydrogen) is shown in fig. 6. We observed expected increasing of $H_2(B^1\Sigma^+_u, v'=3)$ because of increasing of concentration of resonant Ar states.

4. Conclusion

In this work, ro-vibrational spectrum of Lyman system was observed in hydrogen and hydrogen-argon mixture in continuous DC discharge at pressures 80 Pa and 400 Pa. We compared rotational temperatures of Lyman system, Fulcher-α system and the second positive system of nitrogen from nitrogen impurities. We concluded that rotational temperature of second positive system of nitrogen is equal to gas temperature 440 K at both pressures. States of molecular hydrogen were not thermalized. Standard procedure for determination of gas temperature from molecular hydrogen emission systems showed overestimation of temperature in comparison with gas temperature. This effect was observed in Fulcher-α system. We have not found simulation of Lyman system based on the conventional description of the diatomic molecules spectra analysis before, so further investigation has to be made for more precise conclusions. Increasing of $H_2(B^1\Sigma^+_u, v'=3)$ states with increasing of amount of argon was observed in emission spectra of Lyman system because of resonance reactions with resonant Ar species.

Acknowledgment

The authors thank for financial support from the Scientific Grant Agency of the Slovak Republic (VEGA) under the contracts No. 1/0914/14 and 1/0925/14. This work has been carried out within the

framework of the EURO fusion Consortium and has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement number 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

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