G Sergienko et al.

Hydrogen isotope ratios measurements by Penning gauge spectroscopy of molecular Fulcher-? band

Hydrogen isotope ratios measurements by Penning gauge spectroscopy of molecular Fulcher-α band

Gennady Sergienko, Sebastijan Brezinsek, Alexander Huber, Michaele Freisinger

Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung – Plasmaphysik, Partner of the Trilateral Euregio Cluster (TEC), 52425 Jülich, Germany

Abstract

Penning gauge spectroscopy of Balmer-α lines of hydrogen isotopes is widely used in fusion experiments to determine the hydrogen isotope ratios and the partial pressures in the pump duct. The Balmer-α line isotopic shifts are very small < 0.176 nm and the lines partially overlap because of the presence of energetic atoms produced by molecular dissociation. The ro-vibrational emission bands of each hydrogen isotopomer consist of many narrow spectral lines, covering a wide wavelength span and have an unique signature. To investigate the capability of the hydrogen molecular spectroscopy for the isotopic ratio determination, an Alcatel-type Penning gauge was coupled by the optical fiber to the Echelle spectrometer having 365 - 715 nm spectral range and the spectral resolving power above 20000. The intensities of both atomic Balmer-α lines and molecular Fulcher-α bands were measured in the range of $6 \cdot 10^{-6}$ - $4 \cdot 10^{-3}$ mbar. The rotational and vibrational populations were almost independent of the gas pressure below $2 \cdot 10^{-4}$ mbar. The total intensities of the Fulcher-α molecular bands were linearly proportional to the gas pressure. The H_2 and D_2 molecular emission in 599 - 639 nm spectral range were in a good agreement with the isotopic composition of the used gas mixtures.

Keywords: Penning gauge spectroscopy; Balmer-α line emission; Fulcher-α molecular band emission, hydrogen isotope gas mixture.

1. Introduction

ITER and DEMO will use a optimum 50%:50% deuterium-tritium gas mixture as fuel. These mixtures are important to monitor both in the confined fusion plasma itself and in the pump ducts because the fusion reaction rate depends on the hydrogen isotope ratios. Penning gauge spectroscopy of Balmer-α lines of hydrogen isotopes is one of the diagnostics which is used to determine the hydrogen isotope ratios and the partial pressures in the pump duct. Such a diagnostic system is also foreseen in ITER [1]. The Balmer-α line isotopic shifts are very small: ≈ 0.176 nm for hydrogen/deuterium lines and ≈ 0.059 nm for deuterium/tritium lines. In addition, these lines are partially overlapped because of the presence of energetic atoms produced owning to molecular dissociation. The molecular ro-vibrational emission bands of each hydrogen isotopomer consists of many narrow molecular lines, covering a wide wavelength span and have an unique signature, which allows to discriminate better the spectral emissions of different isotopomers. The molecular spectroscopy can provide an additional information such as the molecular hydrogen isotopomer ratios, which could be important for plasma-wall interaction study. Another hand, the molecular emission spectra of the Penning discharge have essentially low line intensities in comparison with atomic hydrogen lines from the most prominent Balmer series.

In contrast to our previous study [2], the present paper is focused on the investigation of the capability of the hydrogen molecular spectroscopy to determine the hydrogen isotopic ratio in Penning gauge plasma.

2. Experimental set-up

The vacuum system shown on the figure 1 was the stainless steel vacuum chamber with the total volume of about 20.2 liters. All vacuum flanges were ConFlat type with oxygen-fee copper gasket. To reduce hydrogen inventory and a minimum vacuum pressure, only metal was used for the in-vacuum components, that was the major improvement in comparison with the vacuum system used in [2]. The exceptions were the quartz vacuum window for the Penning gage, the ceramic insulators and the Viton o-rings in the vacuum valves. The system was evacuated with the 360 l/s (nitrogen gas) turbomolecular pump, which was connected to a dual-stage, rotary vane pumps with a pumping speed of 1.7 l/s. The base vacuum pressure without the system heating was about $2 \cdot 10^{-8}$ mbar. Partial pressures of hydrogen and deuterium were varied by the change of hydrogen and/or deuterium gas flows using the precision leak valves. The pressure in the vacuum system has been monitored by means of: a hot cathode ionization gauge, a thermal conductivity gauge and two capacitive vacuum gauges (Baratron type). The capacitive vacuum gauges having different measurement ranges $10^{-4} - 1$ mbar and $10^{-5} - 0.1$ mbar were mainly used for setting of the desired hydrogen/deuterium composition and the pressure of the gas mixture. The Alcatel Model CF2P Penning gauge in the combination with Alcatel ACF111 power supply was used to detect hydrogen and deuterium by means of both atomic and molecular spectroscopy. The Penning gauge was mounted on the port, which was at 90° angle with respect to the gas injection port, in the vicinity of the capacitive vacuum gauges to minimize the pressure differences.

The plasma of the Alcatel Penning gauge was observed thru the quartz vacuum window of Ø32 mm by means of collecting optics shown on the figure 2. Two achromatic lenses with focus lengths of 100 mm and 25 mm coupled the plasma light to Ø600 µm quartz optical fiber having NA=0.22. This optical arrangement illuminates more homogeneously the fiber entrance and reduces the influence of plasma volume changes on the line intensity measurements. The observation volume coves both plasma cells of the Alcatel Penning gauge, which has the transverse dimensions of about 18×10 mm^2 . The exit of the optical fiber was connected to the high resolution Echelle spectrometer (Spectrelle 20000, Systematix and GWU Lasertechnik GmbH cooperation) having resolving power $\lambda/\Delta\lambda \sim 20000$ and equipped with the 1024×1024 pixels camera (Andor iXon[EM]). The spectrometer covers 365 - 715 nm spectral range, that allows to measure simultaneously atomic and molecular hydrogen spectra, and has high throughput (F-number of 3.6) over about 45000 spectral channels. Unfortunately, the étendue of this device is quite small about $1.7 \cdot 10^{-4}$ mm$^2 \cdot$sr, for this reason long repetitive exposures in the range of $360 \times 10 - 0.5 \times 10$ s were required to measure both atomic and molecular hydrogen spectra within the pressure range of $10^{-5} - 10^{-3}$ mbar. The spectrometer with the collection optics was calibrated with help of a standard calibration source.

3. Measurements and discussion

The measurements of Fulcher-α band emission ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$) in the 600 - 640 nm spectral range were performed for deuterium, hydrogen and different deuterium-hydrogen gas mixtures. The examples of the spectra measured in the Penning gauge plasma are shown on figure 3. Fulcher-α band was chosen because it was successively used previously for the measurements of the molecular fluxes in the edge plasma [3-5]. Only Q-branches of Fulcher-α band emission ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$) were used for data analysis. The diagonal transition with the vibrational quantum numbers $v'=v''=$ 0 - 3 and $v'=v''=$ 0 - 5 respectively for molecular hydrogen and molecular deuterium were analyzed. The rotational population of the $d^3\Pi_u^-$ vibrational levels were derived in a standard way [3- 5] from Boltzmann plots of the intensities of the rotational lines normalized to corresponding transition probabilities and degeneration factors versus rotational energy difference with respect to rotational level with rotational quantum number N=1. The rotational temperature was calculated by using intensities of the first 5 rotational lines for each vibrational level, which are shown on figure 3. The pressure dependency of the rotational temperature for hydrogen and deuterium molecules is

shown on the figure 4. The highest rotational temperature was observed for both hydrogen and deuterium molecular $d^3\Pi_u^-$ $v''=0$ levels. The rotational temperatures were almost constant within the error bars for the gas pressures below $2 \cdot 10^{-4}$ mbar (the corresponding values are shown on the Table 1) and increases maximum by about 65 K for all measured vibrational levels at higher pressures. The rotational temperature of the hydrogen molecules increases monotonically in contrast to the rotational temperature of the deuterium molecules, which reaches its maximum at the gas pressure of about $2.4 \cdot 10^{-3}$ mbar and then reduces. The sum of the measured vibrational line intensities, which were found with help of the measured rotational temperatures, as a function of the gas pressure are shown on the figure 5. The all intensities were well proportional to the deuterium gas pressure below the pressure 10^{-3} mbar. A small increase of the molecular deuterium line intensities appeared above this pressure. The relative vibrational level population of the $d^3\Pi_u^-$ electonic state derived with help of the molecular data from [6] did not change with the pressure within the measurement errors. The measured relative vibrational populations averaged over the pressures are shown on the figure 6 together with its theoretical values. The theoretical $d^3\Pi_u^-$ populations were calculated with the help of the Franck–Condon factors from [6] under the assumption of the direct excitation from the electronic ground state $X^1\Sigma_g^+$. The $X^1\Sigma_g^+$ vibrational level population was described by the Boltzmann distribution with the vibrational temperatures equal to the rotational temperatures of the ground state $Trot(X^1\Sigma_g^+) \approx 2 \cdot Trot(d^3\Pi_u^- \, v''=0)$. The deviation of the measured $d^3\Pi_u^-$ vibrational population from calculated one can be completely eliminated by introducing an additional vibrational level populations of about 4%-18% (with respect to $X^1\Sigma_g^+$ $v=0$ level population) for the vibrational levels lying between 2.2 eV and 3.6 eV of the ground state vibrational energies as shown on figure 7. This overpopulation of the $X^1\Sigma_g^+$ vibration levels is probably due to the interaction of the excited molecules or/and molecular ions with the metallic surfaces of the electrodes.

The Balmer-α line intensities have the linear dependence versus the gas pressure below $4 \cdot 10^{-4}$ mbar as seen on figure 8. The H_α/D_α line intensity ratio is 1.36 ± 0.04 at this pressures, which is in a good agreement with the value of 1.28 ± 0.01 measured earlier [2]. The essential decrease of both H_α and D_α line intensities as well as H_α/D_α line intensity ratio appeared above this pressure. The nonlinear behavior of the Balmer-α line intensities is probably due to the volt-ampere characteristic of the Penning gauge power supply, which is shown on the figure 9. The power supply starts the restriction of the discharge power by reducing the discharge voltage when the discharge current reaches about 1 mA at the deuterium gas pressure of about 10^{-3} mbar. The drop of the discharge voltage should result in the reduction of the electron energy. The molecular line intensities are less sensitive to the power supply characteristics because the excitation energy of Fulcher-α band emission is lower the energy required for dissociative excitation of the molecules.

The spectroscopic measurement of the isotopic composition were also performed in the deuterium-hydrogen gas mixtures. A simplified approach based on the independence of the molecular line intensity ratios on the gas pressure in the spectral range 599-639 nm was used because the spectral lines of HD molecules was not observed. The spectra (shown on figure 3) normalized to the its gas pressures were used in a linear combination for fitting of the gas mixture spectra. The fitting coefficients, which are the partial pressures of hydrogen and deuterium gases, were used for the calculation of the isotope composition of the gas mixture. The measurement of $(2.70 \pm 0.04) \cdot 10^{-4}$ mbar H_2-D_2 gas mixture is presented on Table 2, which shows the isotope compositions measured by means of the pressure gauge, the molecular spectroscopy and Balmer-α line spectroscopy. For the calculation of the isotopic composition with help of Balmer-α lines, the H_α/D_α line intensity ratio for pure hydrogen and deuterium gases shown on figure 8 was used for the correction. The H content value provided by molecular spectroscopy is in a better agreement with the isotopic composition of the used gas mixture, which was determined with help of the capacitive vacuum pressure gauge.

4. Summary

   This investigation demonstrates the applicability of the molecular spectroscopy for the determination of the hydrogen isotopomers in the Penning gauge plasma. The ro-vibrational populations of the Fulcher-α molecular band are practically independent from the gas pressures below $2 \cdot 10^{-4}$ mbar. This observation essentially simplify the spectral measurements in the gas mixtures of hydrogen isotopomer because it is not necessarily to measure all ro-vibrational lines to find total intensity of the $d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$ electronic transition, which is required for the partial pressure determination. The intensities of the Fulcher-α band are less affected by the power supply characteristics of the Penning gauge in the comparison with the Balmer-α line intensities. The isotopic composition measured by the molecular spectroscopy is in a good agreement with the actual composition of the gas mixture. For a practical measurement of the H/D content in an unknown gas mixtures by means of the Penning gauge molecular spectroscopy, Fulcher-α band and reference spectra of HD molecules must be also analyzed. The Penning gauge molecular spectroscopy can be also used for the measurement of the tritium contents in deuterium-tritium gas mixtures. For this purpose, the molecular spectra of T_2, HT, DT in the Penning gauge plasma must be investigated and the reference spectra should be produced.

Acknowledgments

References

[1] C.C. Klepper et al., Design of a diagnostic residual gas analyzer for the ITER divertor, Fusion Engineering and Design 96–97 (2015) 803–807.

[2] G. Sergienko et al., Improving accuracy of Penning gauge spectroscopy for the determination of hydrogen isotope H/D ratios, Fusion Engineering and Design 123 (2017) 906–910.

[3] U. Fantz, Emission spectroscopy of hydrogen molecules in technical and divertor plasmas, Contrib. Plasma Phys. 42 (2002) 6-7, 675−684.

[4] S. Brezinsek et al., On the measurement of molecular particle fluxes in fusion boundary plasmas, Journal of Nuclear Materials 313–316 (2003) 967–971.

[5] G. Sergienko et al., Molecular deuterium behaviour in tungsten divertor on JET, Journal of Nuclear Materials 438 (2013) S1100–S1103

[6] U. Fantz and D.Wünderlich, Franck–Condon factors, transition probabilities, and radiative lifetimes for hydrogen molecules and their isotopomeres, Atomic Data and Nuclear Data Tables 92 (2006) 853-973.

Table 1. Rotational temperatures of $d^3\Pi_u^-$ v'' levels.

v''	H_2 Trot [K]	D_2 Trot [K]
0	476±13	405±18
1	390±7	344±18
2	384±13	401±15
3	278±12	383±11
4	-	351±11
5	-	331±28

Table 2. Measured isotopic composition of H_2-D_2 gas mixture with the pressure of $(2.70\pm0.04)\cdot10^{-4}$ mbar.

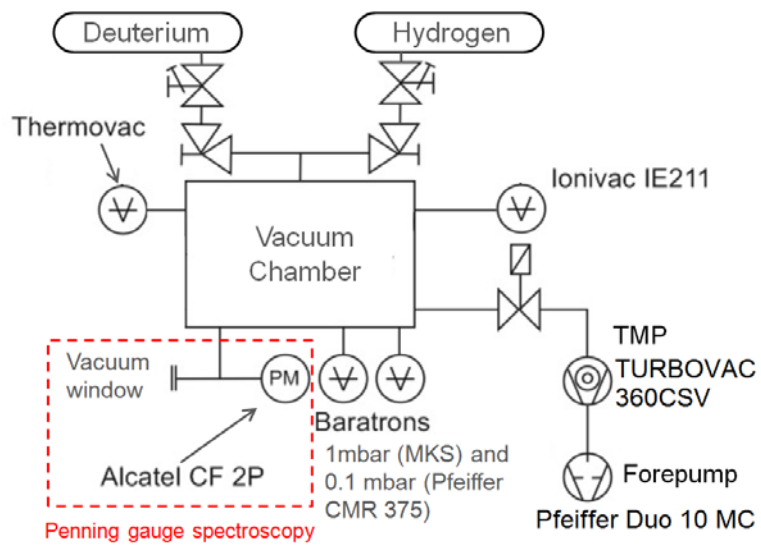| Method	H content [%]
Pressure gauge	54.1±1.4
Molecular spectroscopy	54.9±1.2
Balmer-α spectroscopy:	
H_α/D_α ratio correction	53.7±2.4
no correction	60.9±2.5

Figure captions

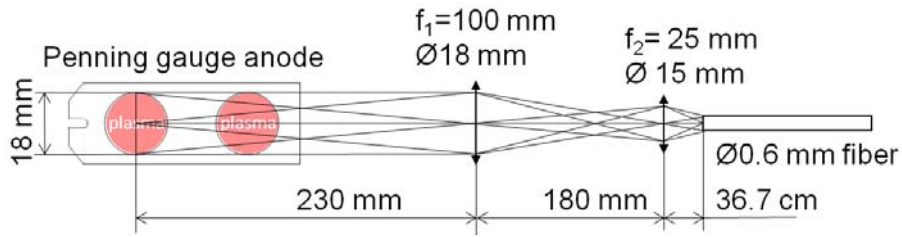Fig. 1. Vacuum system used for Penning gauge spectroscopy.

Fig. 2. Optical system used for the plasma light collection.

Fig. 3. Measured molecular hydrogen and deuterium spectra in the Penning gauge plasma.

Fig. 4. Rotational temperatures of Q-branches of Fulcher-α band diagonal transitions versus the gas pressure.

Fig. 5. Vibrational spectral ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$) line intensities of hydrogen and deuterium molecules versus the gas pressure.

Fig. 6. Vibrational relative populations of the hydrogen and deuterium molecular $d^3\Pi_u^-$ electronic state.

Fig. 7. Relative vibrational population of the electronic ground state $X^1\Sigma_g^+$ versus vibrational level energy.

Fig. 8. H_α and D_α line intensities and intensity ratio versus respectively hydrogen gas and deuterium gas pressure.

Fig. 9. Characteristics of the Alcatel ACF111 power supply.

Fig. 1. Vacuum system used for Penning gauge spectroscopy.

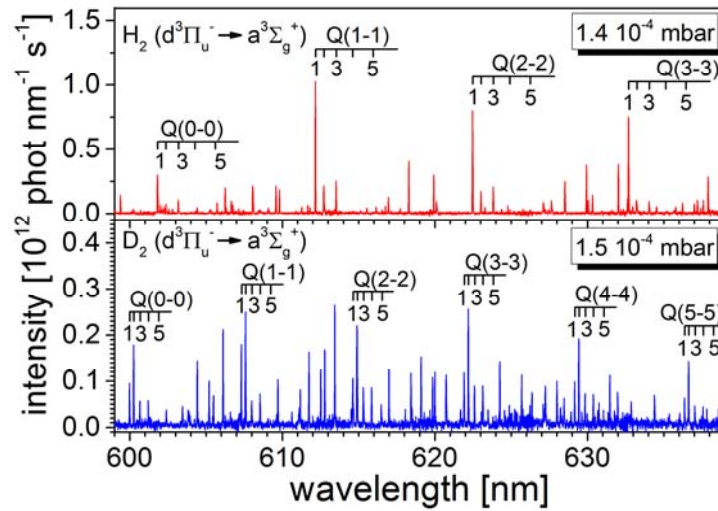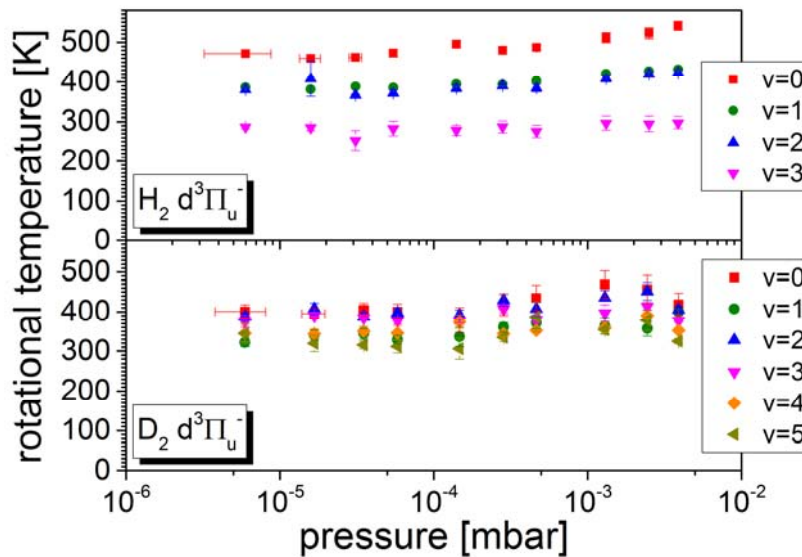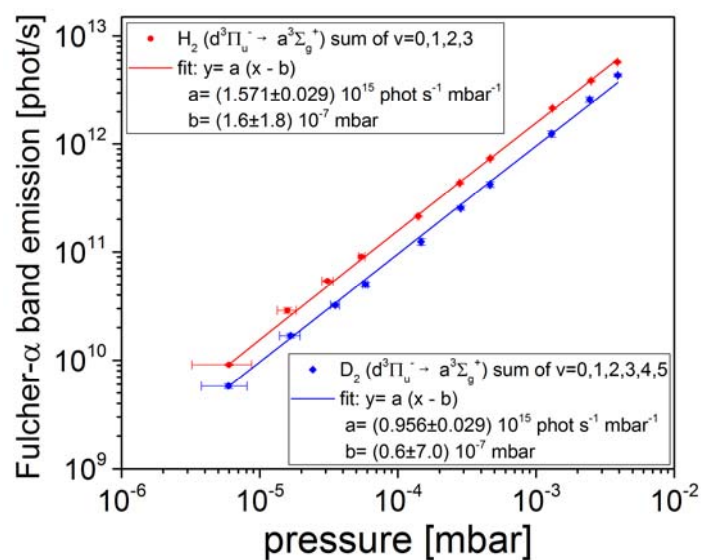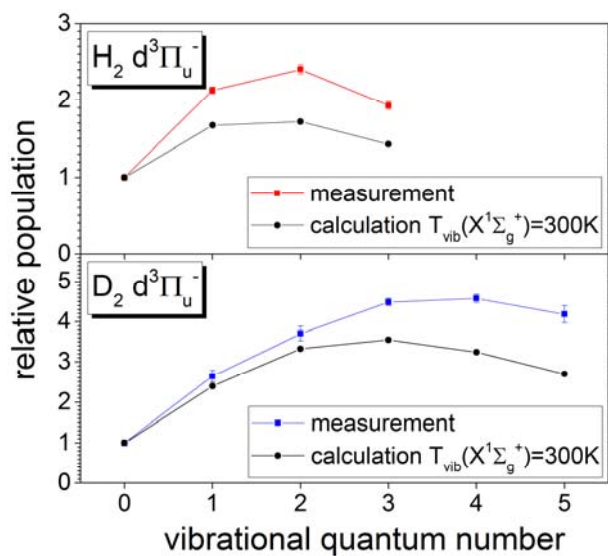Fig. 2. Optical system used for the plasma light collection.

Fig. 3. Measured molecular hydrogen and deuterium spectra in the Penning gauge plasma.

Fig. 4. Rotational temperatures of Q-branches of Fulcher-α band diagonal transitions versus the gas pressure.

Fig. 5. Vibrational spectral ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$) line intensities of hydrogen and deuterium molecules versus the gas pressure.

Fig. 6. Vibrational relative populations of the hydrogen and deuterium molecular $d^3\Pi_u^-$ electronic state.
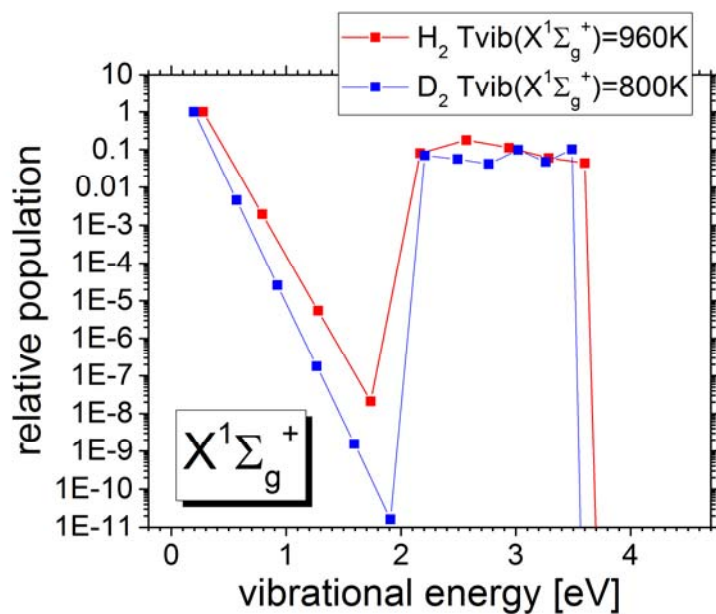
Fig. 7. Relative vibrational population of the electronic ground state $X^1\Sigma_g^+$ versus vibrational level energy.
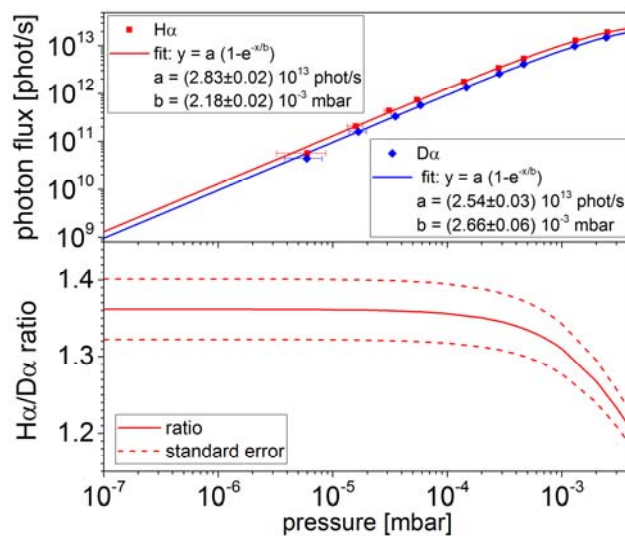

Fig. 8. H_α and D_α line intensities and intensity ratio versus respectively hydrogen gas and deuterium gas pressure.
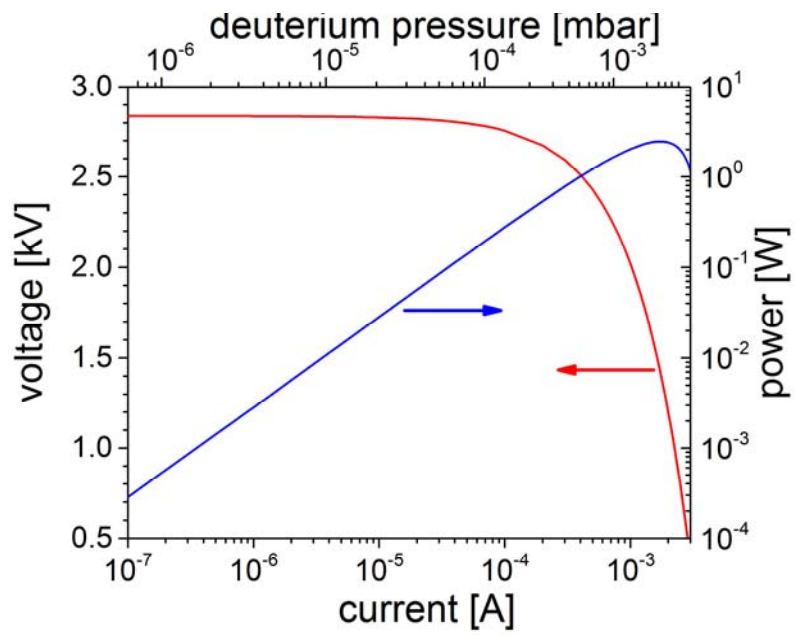
Fig. 9. Characteristics of the Alcatel ACF111 power supply.