Determination of Rotational Temperature from Spectra of the Nitrogen 2nd Positive System at Intermediate Pressures Using Boltzmann Plot

J. Varga[1], J. Jašík[1], P. Macko[1], V. Martišovitš[2], P. Lukáč[1], P. Veis[1]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics,
Comenius University, Mlynská Dolina F2, 842 48 Bratislava, Slovak Republic
[2]KAFZM, Faculty of Mathematics, Physics and Informatics, Comenius University,
Mlynská Dolina F2, 842 48 Bratislava, Slovak Republic
e-mail: *varga@fmph.uniba.sk, veis@fmph.uniba.sk*

Abstract: Optical emission spectroscopy of pulsed modulated radiofrequency (RF) discharge in pure nitrogen at pressures 130 Pa – 15 kPa has been used for observation of the rotational structure of the 2nd positive system. Rotational temperature of plasma has been determined from resolved spectra of rotational structure of the 2nd positive system using Boltzmann plot.

1. Introduction

A lot of reactions are carried on through the electric discharges in gas. There are a lot of consequences – production and destruction of some particles in content. We are studying these processes and their dynamics at present because of understanding and application in practice.

Electron transitions of nitrogen molecule in plasma extending from VUV area with Lyman-Birge-Hopfield system $a^1\Pi_g - X^1\Sigma_g$ (this system is low intense – Einstein coefficient A_{vv} is in range from 15 754 s^{-1} to 17 241.2 s^{-1} [1]) to infrared area with the 1st positive system $B^3\Pi_g - A^3\Sigma_u$ (also low intense – $A_{vv}^{max} \approx 70000\ s^{-1}$ [2]). Homonuclear molecule N_2 does not generate rotational – vibrational transitions in IR area. The most intense bands are in UV or ultra UV area with the 1st negative system $B^2\Sigma_g - X^2\Sigma_g$ of N_2 ($A_{00} = 1.14 \times 10^7\ s^{-1}$ [2], $A^{00} = 1.24 \times 10^7\ s^{-1}$ [2]) and in near UV area also with 2nd positive system $C^3\Pi_u - B^3\Pi_g$. This system is generated by transitions between triplet states and is easy to observe where the nitrogen is excited by electrons. The 2nd positive system is characterized by a high vibrational transition probability and pre-dissociation of levels of $C^3\Pi_u$ state. We can observe this system in arc at low pressures, in plasmatron, in creeping discharge and in DBD reactors.

Accurate quantitative measurements of temperatures and species concentrations in high-temperature air or nitrogen plasmas are important for experimental characteristics of arcjets, radiofrequency or microwave plasma torches, and for the interpretation of reentry flight measurements.

Lofthus and Krupenie have described nitrogen molecular constants and energy levels in detail in their publication [3]. There are potential curves of N_2 and N_2, too. Spectro-

scopic constants are summarized in many publications and the main ones are Suchad and Melzer [4] and Huber and Herzberg [5].

A lot of spectroscopic methods have been developed for rotational temperature measurements from partially resolved rotational structure of vibrational spectra of diatomic molecules by means of numerical simulation of a spectrum for a given experimental arrangement.

Janča et al. [6] projected and used a quick spectroscopic method for determination of the rotational temperature, T_r. They measured the 2nd positive system of nitrogen (transition $N_2(C^3_u, v \quad 2) \quad N_2(B^3_g, v \quad 0)$) in a radiofrequency discharge plasma with frequency 1.5 MHz, power 70 W and gas purity 5.0 in pressure range 30–1500 Pa. They compared this spectrum with the theoretical calculated one. They achieved a very good agreement between theoretical and measured spectra.

Czernichowski [7] calculated the temperature from a partially resolved nitrogen spectrum. He measured the 1st negative system $B^2_u \quad X^2_g$ of ion N_2 with maximum wavelength on 391.44 nm and he determined temperatures in plasma comparing with melded spectra. Thanks to the simplicity this method is very widespread in practice.

Chelouah et al. [8] used the same method for T_r determination. They compared spectra of the 1st negative system $N_2(B^2_u \quad X^2_g)$ and the 2nd positive system $N_2(C^3_u \quad B^3_g)$ of N_2 molecule for temperature range 300–3000 K.

Goyette et al. [9] verified the correctness of the use of the 1st negative system of N_2 ion and the 2nd positive system of N_2 molecule for measuring the temperature. They made their measurements in He–N_2 plasma for pressure range 0.5–1.0 Torr and temperatures 50–800 C. They placed the discharge into the furnace and they were able to have desired temperature of neutral gas with accuracy 3 C. They found out that the rotational temperature determined from the (0–0) band of the 1st negative system linearly increases with gas temperature, however these values were approximately by 150 C higher than the gas temperature. The rotational temperature determined from the (2–0) transition of the 2nd negative system N_2 was not shifted against the kinetic gas temperature and practically this value was identical with the kinetic gas temperature.

2. Experimental Setup

The rotational temperature of nitrogen was measured in pulsed RF 27 MHz nitrogen discharge. Experimental set-up is shown in Figure 1.

We measured the resolved spectra with the rotational structure of the 2nd positive system $N_2(C^3_u \quad B^3_g)$.

The set-up is described in more details in [10,11] except that the DC supply was replaced with RF generator working at 27 MHz with the rectangular modulation (voltage up to 2.5 kV, current up to 250 mA, duration of pulses from 0.2 to 20 ms, duty cycle 1:1) [12]. The pulsed RF discharge was created in Pyrex tube (inner diameter = 17 mm, length = 185 mm) with two quartz windows at the ends. The length of the discharge column was about 100 mm. The RF power was applied to two external ring electrodes. The effective current (ranging from 50 to 250 mA) was measured by a current probe plugged-in to an oscilloscope, which is externally synchronized with the generator. The gas flow, controlled with a mass flow controller (Tesla KA 305), is maintained at 0.3 sccm during all the experiments. The gas pressure (ranging from
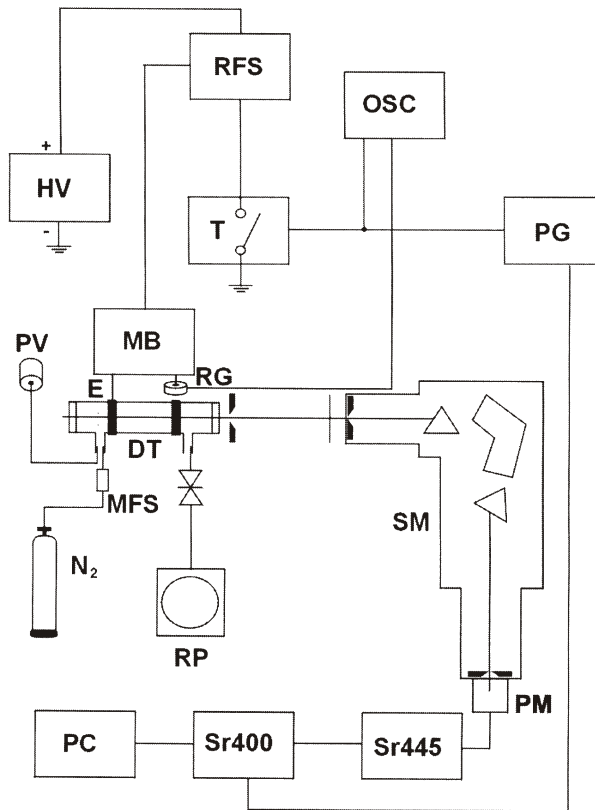
Fig. 1. Experimental set-up. **PV** – piezo gauge Wenzel Electronics PiezoSteel, **DT** – discharge tube, **E** – electrodes, **HV** – high voltage source STATRON, **MB** – matchbox, **MFS** – mass flow controller Tesla KA 306, **OSC** – oscilloscope, **PC** – computer, **PG** – generator of TTL pulses trigger, **PM** – photo-multiplier HAMAMATSU R2949, **RG** – current probe, **RFS** – RF 27 MHz generator, **RP** – rotary pump VS 35 B, **SM** – spectrometer ISP-51, **SR400** – photon counter, **SR445** – preamplifier, **T** – pulse modulation.

130 Pa to 10.3 kPa) is adjusted by a valve situated downstream the tube. The pressure is measured by the piezo gauge (PiezoSteel) upstream the tube.

The light emitted from the axis of the discharge tube is analyzed by a spectrometer with three glass prisms (ISP-51). The spectrometer is equipped with a photo-multiplier tube (Hamamatsu R 2949). Photon counting is performed by a photon counter (Stanford Research Systems SR 400).

3. Experimental Results

The object of our study was to determine the rotational temperature in a pulsed 27 MHz nitrogen discharge from rotationally resolved spectra of the 2nd positive system $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$.

Experimental conditions:

the operating voltage U = 2.6 kV

the pressure range p = 130 Pa – 10.3 kPa.

Figure 2 shows spectra of the 2nd positive system $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$.

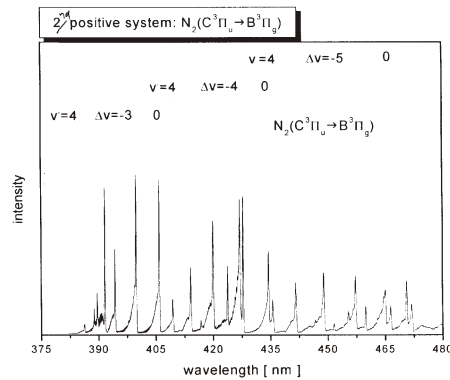For recording of this spectrum we count photons during the first 500 s of discharge.

Fig. 2. Imaging spectra of the 2nd positive system $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ (pressure p = 130 Pa).

The 1st positive system is dominant in the visible and near infrared spectral range and it is profitable for study of state $N_2(B^3\Pi_g)$ emission and state $N_2(A^3\Sigma_u)$ absorption. However, in the range from 350 nm to 500 nm emission of 2nd positive and 1st negative system dominate.

4. Determination of Rotational Temperature

There are more possibilities how to determine the rotational temperature, T_r, from the spectrum of rotational structure of molecule N$_2$ (and other two-molecule gases, too).

One method is to compare the experimental spectra with the simulated one for different T_r with condition of a well-known resolving power of apparatus. This method gives relatively exact results without direct calculations and is useful for not very well resolved spectra.

The second method is suitable for very good resolved spectra. We can calculate the population of each rotational level from the intensities of each rotational transition and then determine the rotational temperature from the plot of the level density as a function of the rotational quantum number, which obeys the Boltzmann distribution law [9,13]. There can be some problems when determining the T_r by this method because of repopulation of present metastable states. For example, in mixture of argon and nitrogen, where we determine the temperature from the second positive system, there can be two slopes in the Boltzmann plot corresponding to two different temperatures, while the kinetic temperature of gas is only one. We recorded spectra of rotational structure of vibrational transition 0–3 and 1–4 of the 2nd positive system $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)$ in wavelength range from 392 to 407 nm for determination of rotational temperature of upper state $C^3\Pi_u$. Figure 3 shows the measured spectra for different pressures.
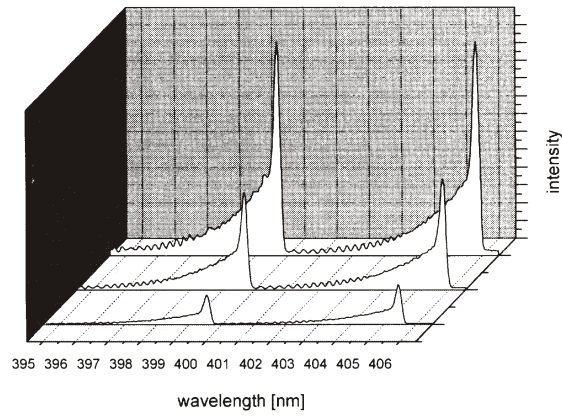
Fig. 3. Experimental spectra of state $N_2(C^3_u, v\ 3)$ for pressures p = 2, 5.8, 10.3 kPa.
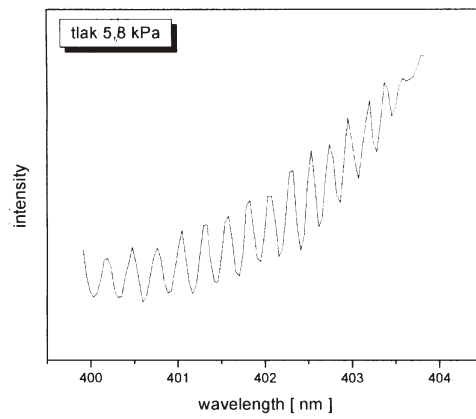

Fig. 4. Example of resolved rotational structure of transition $N_2(C^3_u, v\ 3)$ for pressure 5.8 kPa.
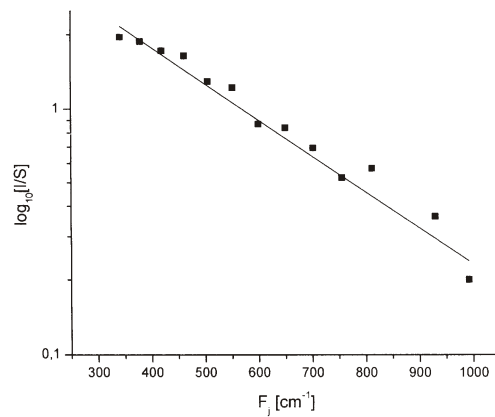

Fig. 5. Typical Boltzmann plot for transition $N_2(C^3_u, v\ 0)$ $N_2(B^3_g, v\ 0)$ and pressure 0.13 kPa. The corresponding rotational temperature for this plot is T_r = 740 K.

Figure 4 shows rotational structure of transition $N_2(C^3_u, v\ 3)$ for pressure 5.8 kPa. We used these structures (for pressures 0.13, 2, 4.1, 5.8, 9.2, 10.3 kPa) for determination of rotational temperature in wavelength range from 394.5 to 403.5 nm.

We determined the rotational temperature of the upper state from the Boltzmann plot [14]. Figure 5 shows the Boltzmann plot for pressure 0.13 kPa and transition 0–3. We used the rotational lines of the 2nd positive system $N_2(C^3_u, v\ 0)\ N_2(B^3_g, v\ 3)$ and $N_2(C^3_u, v\ 1)\ N_2(B^3_g, v\ 4)$ for this calculation. The results we calculated by this method are shown in Figure 6.
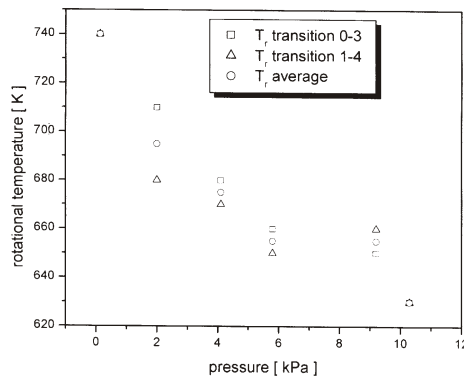
Fig. 6. Dependence of rotational temperature T_r versus pressure given from $N_2(C^3_u, v\ 0)\ N_2(B^3_g, v\ 3)$ and $N_2(C^3_u, v\ 1)\ N_2(B^3_g, v\ 4)$.

5. Conclusion

In this paper, we present the measurements of rotational temperature from the 2nd positive system $N_2(C^3_u)\ N_2(B^3_g)$ for the transitions $v\ 0\ v\ 3$ and $v\ 1\ v\ 4$, respectively. Rotationally resolved spectra were observed for J ranging from 18 to 34. So the rotational temperature has been evaluated from the Boltzman plot for the pressure range from 0.13 to 10.3 kPa. Our measured rotational temperature decreases from 740 to 630 K with increasing pressure. In the future we plan to compare this rotational temperature measurements with temperature evaluated from a comparison of modulated and experimental spectra of non-rotationally resolved 2nd positive system for J < 18.

Acknowledgements

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