

Study of N₂ Plasma Generated by RF Discharge. Nitrogen – First Negative and Second Positive System Investigation

V. Foltin, J. Jašík, J. Varga, P. Čermák, P. Macko, P. Veis

Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University,
Mlynská dolina F2, 842 48 Bratislava, Slovak Republic, e-mails: veis@fmph.uniba.sk

Abstract: In this work we investigate the effect of pressure on the rotational temperature of N₂ in the RF discharge plasma. Optimal pressure for the ionization has been found by analyzing spectra of the First negative system and the Second positive system. Detection was carried out in the newly built detection system based on CCD.

1. Introduction

In gas discharges electron-molecule or electron-atom collisions are powerful enough to produce excited particles in a state that is different from the ground one. During de-excitation these particles may emit photons that can be observed and analyzed. This phenomenon is utilized at any kind of spectroscopic investigation. Using this method we can gain much important information about composition, energy distribution, etc. in discharge.

In case of molecules, excitation in a given electronic state is spread over the rotational and vibrational levels but emission of light is possible only if the quantum selection rules are obeyed. If rotational and vibrational populations are distributed according to the Boltzmann distribution, rotational and vibrational temperatures of gas can be estimated. In the case of non-equilibrium plasma such temperatures are, in general, different from the kinetic temperature of the gas and can also be different from each other. Therefore the estimated temperatures are not thermodynamic temperatures in the sense of equilibrium.

In the case of higher pressure collisions between the neutral and the excited molecules are sufficiently effective and there is a tendency of rotational temperature to equilibrate with the kinetic temperature of the heavy species. For example, rotational temperature measured at the higher pressure on the (0–0) band of the first negative system (FNS) of N₂⁺ at 391.4 nm can be considered as a kinetic temperature of the gas into which nitrogen was introduced as an impurity [1]. In certain conditions electric discharge can produce a plasma in which different species do not have sufficient time to thermalize themselves. Such non-equilibrium plasma is characterized by electron temperature which is much higher than the rotational one. The properties of such a plasma are relatively well known and have been exploited in several fields (such as laser technology, surface treatment and pollution control).

Measuring the plasma temperatures gives access to information concerning the chemical reactivity of the medium and the thermal energy produced. The rotational temperature of the excited nitrogen species corresponds roughly to the temperature of the neutrals whereas a high apparent vibrational temperature is indicative of a vibrationally excited species that is chemically reactive. Thus the rotational and vibrational temperatures are important parameters to consider in any plasma application.

There are many various techniques for estimation of rotational temperature. Among them, most widely used is that of the Boltzmann plot. In principle temperature is determined from intensity of well-resolved rotational transition peaks. However, lines of rovibrational spectra are usually very close to each other, so we can observe isolated peaks only in the "tail" (depends on instrument resolution) of spectra. As we shall discuss later determination rotational temperature only from a part of spectra may lead to unreliable and incorrect results. On the other hand there is a more complex method for determination of rotational temperature. It consists of simulating whole rovibrational spectra as a function of temperature and experimental conditions and comparing it to the experimental one. In this way, we can exploit all the experimental data and avoid mistakes in estimation of rotational temperatures.

1.1. Estimating T_r from synthetic model

The measurement of plasma temperature is based on the comparison of the experimental and theoretical spectra. Theoretical construction of the spectra of neutral and ionized molecules of nitrogen is partially based on the analysis performed by Hartman and Johnson [2]. Sequence of the following steps should be realized. Firstly, the wavelength of each spectral component should be determined in terms of five quantum numbers (J' , J'' , v' , v'' , g) where: J and v are the rotational and vibrational quantum numbers, respectively;

g is the multiplicity factor. A single prime represents the upper level and the double prime the lower one. Afterwards, as input parameters, rotational and vibrational temperatures, are given and population of upper level is calculated for them from the Boltzmann distribution for the given temperatures. Finally, from the known population of the upper level a synthetic spectrum as a set of spectrum intensities $f_i(T_r, T_v, \dots)$ is computed at selected wavelengths λ_i [3–5]

$$f_i(T_r, T_v, \dots) = \text{const.} \cdot \frac{g_j}{2J_j} \frac{J_j}{1} n_j(T_j, T) G(\lambda_i, \lambda_j)$$

where λ_j , λ_i and J_j are the frequency, the Höln-London factor and the rotational quantum number of the corresponding upper state level. Convolution of the physical line shape and instrument function (with parameter Δ) is represented by function $G(\lambda_i, \lambda_j)$.

The rotational temperature (T_r) is commonly determined by one of the following methods:

1. The first method consists in minimizing the surface delimited between the experimental and simulated spectra. The most convenient way consists in constructing the plot giving dependence of $\Delta S/S$ on the rotational temperature (which was inserted as the input parameter), where S is the total surface delimited by the spectral band within the chosen window and ΔS is the surface trapped between the two spectra [5]. When ΔS varies monotonically

with the trial value of rotational temperature T_r and crosses the zero value on the axis at a clearly defined point, this point gives the actual rotational temperature.

2. The second method [6] consists in minimizing the ratio (σ/k_m) , where σ is the standard deviation of k_m defined by the relation:

$$k_m = \frac{1}{N} \sum_{i=1}^N \frac{I_e(\lambda_i)}{I_s(\lambda_i)}$$

where I_e represents the experimental and I_s the simulated intensity of the light corresponding to the wave length λ_i , N_i represents the total number of discrete values of the spectral intensities considered in the part of the band in which the criterion is applied.

A comparison between the results obtained using those two criteria for the measured spectra shows that the two evaluations are quite identical. However, in the case when signal to noise ratio is not sufficiently high, the two evaluations diverge. This occurs when experimental and calculated spectra profiles intersect each other in several places, whereas they ought to follow each other smoothly. In work [6] about the laser ablation of graphite the vibration temperature T_v and rotational temperature T_r are calculated in a way similar to the second method but there the expression is minimized

$$S^2(T, T_r) = \frac{\sum_{i=1}^N [I_i^{\text{exp}} - I_i^{\text{sim}}(T, T_r)]^2}{N(N-1)}$$

in which spectral intensities are I^{exp} , I^{sim} for the experiment and simulation, respectively. The same distribution of points N is applied for experiment and for simulation curve.

1.2. Field of use

The temperature of neutral gas is often determined via evaluation of the shape of rotational spectra of two-atomic molecules present in plasma. Nitrogen molecule and its ion are commonly used for this purpose. The rotational level distribution of a certain electronic and vibronic state can be measured by several methods, among them optical emission spectroscopy, laser-induced fluorescence, Raman scattering, etc. In certain conditions rotational temperature reflects the neutral gas temperature more reliably than the translational temperature measured by the Doppler broadening [7]. Only if the lifetime of the excited molecule is long enough for thermalisation, the rotational level population represented by the emission band reflects the neutral gas temperature. This is the case for:

- a) high enough pressures with high collision rates (even if the lifetime is significantly reduced due to collisions)
- b) metastable molecule states, such as $N_2(A^3 \Sigma_u^-)$ [8].

However, in a low pressure plasma emission of light commonly occurs before the thermalisation of the rotational level population of the electronically excited state. Therefore the observed population of the rotational levels is determined by the excitation mechanisms and by the rotational level population of the electronic states from which the upper electronic state of the chosen molecule band is populated. For a correct temperature determination all the excitation channels must be considered [9–11]. This fact is often ignored in literature, where only the following situations are considered:

- a) direct population by electron impact [6, 12]
- b) rotational level distribution of the excited molecule is simply assumed to be a Boltzmann distribution according to the gas temperature [13, 14];

It was shown in [15] that for the 0-0 band of the first negative system (FNS 0-0) of the N_2^+ ion at least two excitation channels have to be considered in order to obtain a reliable measure for the gas temperature:

- a) one excitation channel results in a rotational level distribution according to the neutral gas temperature;
- b) the second excitation channel is connected with rotational excitation and, thus, the rotational temperature of so generated molecules is much higher than the gas temperature. In this case the fitting spectra assuming only one single Boltzmann would lead to too high rotational temperature. Therefore the two-temperature model has to be used.

2. Experiment

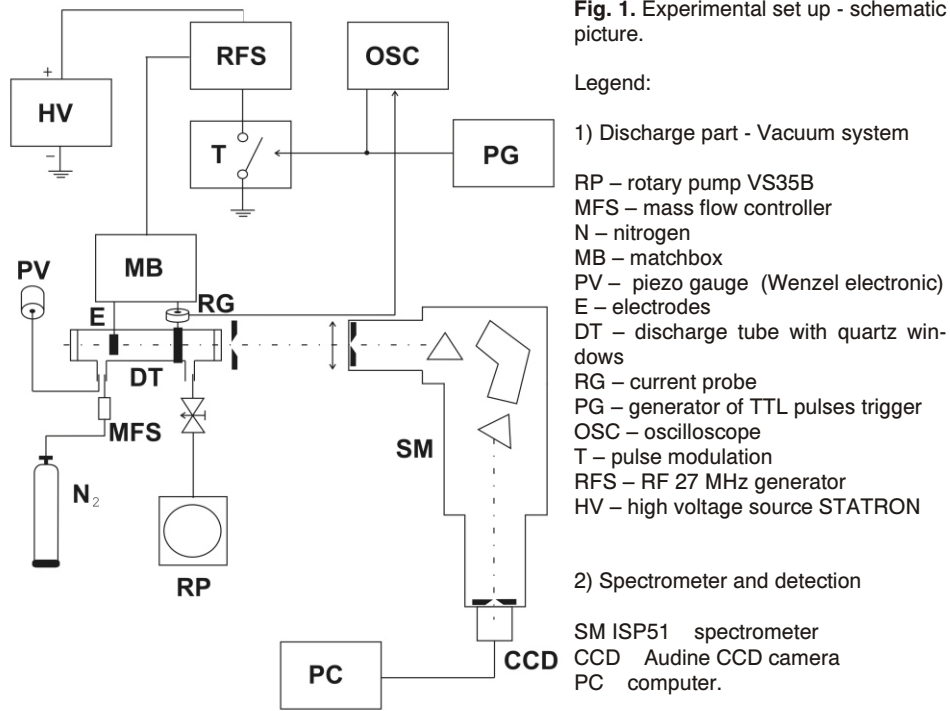
The goal of presented paper is to carry out, for the first time, the following with the upgraded experimental setup:

- measurement of Nitrogen First negative system spectra for determining the rotational temperature based on the comparison of experimental and simulated spectra in LIFBASE [16];
- comparison of behaviour of recorded FNS and SPS spectra.

All the experiments were carried in our upgraded experimental setup for the diagnostics of plasma processes [17–20] where, instead of PMT detection part, a new CCD detection system was designed and utilized. Experimental setup consists of the parts: 1) Discharge part, 2) Spectrometer and Detection. Since the first part was precisely described earlier [17–20], we will concentrate on the second one.

Our spectrometer runs now with CCD camera system which was built according to Audine project [21]. It allows us to use different CCD chips from the Kodak KAF series [22] for the recording of spectra. Based on the parameters like quantum efficiency curve, photosensitive area etc. all of these chips, incl. the basic one KAF 401 are sufficient for the presented experiment. For this paper spectra were recorded by KAF 401 chip with a photosensitive area (6.91 × 4.6) mm which represents the following set of pixels: (horizontal 768, vertical 512; pixel size 9 μm). Within the Pisco software [22] pictures are recorded during the experiment and converted to the regular spectra so that final spectra can be further evaluated. To minimize the signal to noise ratio our CCD camera is cooled all the time from the backside and the space between CCD chip and output window from the spectrometer is evacuated. In the light paths from the plasma reactor quartz windows were used.

Plasma generation part of our experimental setup was described previously [17–20]. The rotational temperature of nitrogen was measured in the nitrogen plasma generated by pulsed RF 27 MHz discharge. Emission spectra at different pressures (in a sequence from the vacuum up to the vanishing of discharge due to the high / breakdown pressure) within the same flow of nitrogen were recorded. Experimental setup is shown in Fig. 1.



3. Results and Discussion

In our work rotational temperature for investigated nitrogen first negative system (FNS 0-0 band) was estimated after processing set of all simulated spectra within LIFBASE [16] by the procedure based on the comparison of the area between experimental and simulation spectra. Spectra for all rotational temperatures in the range from 10K to 2000K within the temperature increment of 5K were simulated. For all peaks, occurring in our case from 389.4 nm to 390.74 nm, their areas (M_i measurement, C_i simulation) were calculated. The simulated spectrum, for which the minimum of the difference of those areas (i.e. $\min |M_i - C_i|$) occurs, will be considered as the best and the rotational temperature will be assigned from it.

Since the experimental and simulated spectra were differently normalized, normalization factor k , which is different for each rotational temperature, needs to be calculated. In that case we define:

$$f(k) = \sum_{i=1}^n (kC_i - M_i)^2 \quad (1)$$

where n is the number of peaks, C_i is the area for the i -peak of simulated spectra, M_i is the area for the i -peak of experimental spectra and k is the normalization factor which needs to be calculated. In order to determine a rotational temperature from experimental spectra, we are looking for the minima of $f(k)$, i.e. for:

$$\frac{df(k)}{dk} \sum_{i=1}^n 2C_i(kC_i - M_i) = 0 \quad (2)$$

Then, from (2), for the normalization factor k we have

$$k = \frac{\sum_{i=1}^n C_i M_i}{\sum_{i=1}^n C_i^2} \quad (3)$$

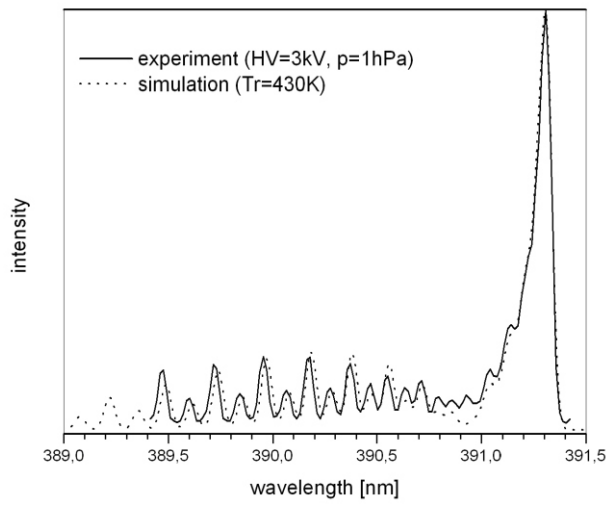


Fig. 2. First negative system of nitrogen. Comparison of experimental and simulated spectra. Experiment: pressure 1hPa, discharge high voltage 3kV; Simulation: $T = 430\text{K}$.

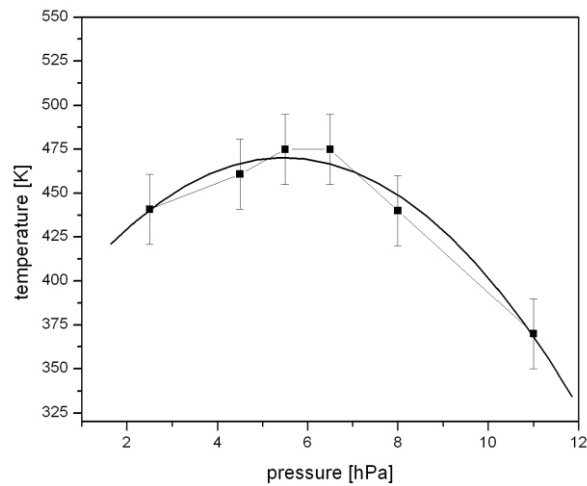


Fig. 3. Assigned rotational temperature as a function of pressure.

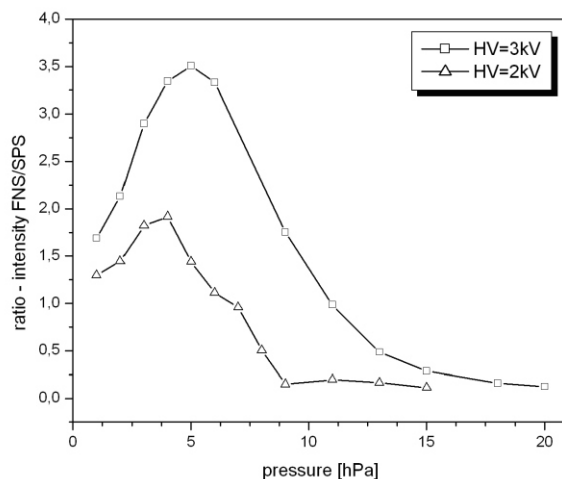


Fig. 4. Ratio of the intensities FNS/SPS as a function of pressures.

During the experiment both systems First negative and Second positive of nitrogen were detected. Based on the analysis of the pressure dependence for the ratio of the signal at the head of peaks for the investigated systems (Fig. 4) we present here the following interpretation: In the region of low pressures (i.e. 0–5 hPa; HV = 3 kV) there the FNS to SPS ratio increases with the increasing pressure in the favour of the FNS since there is a lack of ions and electrons meet fewer targets on their paths and more of them impact the walls of the tube. The case of the high pressure (i.e. above 7 hPa, HV = 3 kV), up to the point at which discharge is switching off due to the “overpressure”, corresponds to situation when electrons have short mean free paths and the FNS to SPS ratio decreases. In between these regions there exists the maximum corresponding to optimal ionization (peak in Fig. 4). These findings correspond also to the behaviour of assigned rotational temperature (Fig. 3).

4. Conclusion

Our finding can be summarized as follows: Firstly, we have proved many advantages of the used measurement technique with upgraded detection system. Applications of CCD chip in emission spectroscopy allow us to gather all rovibrational spectra in a short time so the time evolution of the system can be observed. Also, unlike a standard photomultiplier measurement, we are not bound to certain wavelength (or short interval) but we have a wide spectral range (depending on the chip, cca. 400–900 nm). Secondly, the ratio between Nitrogen first negative and second positive systems as a function of pressure has been observed (Fig. 4) and its behaviour corresponds to the pressure behavior of the assigned rotational temperature. In this case those systems can be considered as representatives of ions and neutral particles, respectively. Discharge working conditions for the sector of maximal ionization were obtained. We estimate an important role of this sector and fine adjustment of discharge for the further study of plasma induced processes. Based

on the presented results further experiments with the goal to increase spectral sensitivity, resolution and to test similar gas systems (first of all, gases obtaining nitrogen) will be studied. We are in a process of construction and further upgrading of:

- the competitive discharge system - flowing afterglow microwave discharge which produces "clear plasma" in the frame of VEGA 1/3043/06;
- our spectroscopic facilities (e.g. sensitivity increase within ICCD camera and construction of VUV spectrometer, also in the frame of VEGA 1/3044/06.

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