

NEW DATA CONCERNING THE NITROGEN 2^+ AND 1^- BANDS SYSTEMS EXCITATION IN A CYLINDRICAL HOLLOW CATHODE PLASMA IN He + N₂ GASE MIXTURES

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We present some new data concerning the specific excitation of the 2^+ and 1^- nitrogen band systems in a hollow cathode plasma in N₂ + He gas mixtures. The relative intensities of the band heads of these both systems and of He spectral lines distributions versus the partial N₂ pressure in the N₂ + He gas mixtures, and the upper vibrational excited level population against the same parameters give us a good representation about the stimulation or inhibition of the nitrogen 2^+ and 1^- bands excitation.

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1. Introduction

The relative intensities behaviour of some N₂ bands like the second positive 2^+ ($C^3\Pi_u - B^3\Pi_g$) and the first negative 1^- ($B^2\Sigma_u^+ - X^2\Sigma_g^+$) systems in several conditions are of great importance in some special physical processes, plasma chemistry, astrophysics, etc.

Due to a remarkable electric current amplification and a dominant nonmaxwellian electrons energy distribution function (here we have 2 – 3 groups of electron energies [1]) having the possibility to excite a great variety of N₂ and N₂⁺ vibrational levels.

So we have had the opportunity to estimate and to represents N₂ and N₂⁺ vibrational levels populations against the gas pressures. In some cases the N₂ and N₂⁺ vibrational levels concentration behaviours are not the same as the band heads relative intensities, coming from these levels.

2. Experimental

The excitation of N₂²⁺ and N₂¹⁻ bands systems in N₂ + He gases was made in a cylindrical hollow cathode electric discharge plasma.

The cylindrical cathode and the anodes were of cooper metal (the cooper cavity has an inner diameter of 6 mm and a length of 30 mm), water-cooled, on the purpose to avoid the thermal influences on the electric and spectral measurements. The partial set up was presented in an earlier paper [2]. The electric discharge tube was connected to a conventional vacuum pump.

The gases pressures were varied in the range of 0,5 – 10 torr, the voltages in the range 200 – 400 Volts and the electric current intensity 0 – 250 mA. In the experimental set-up we had an SPM-2 Zeiss 650 tr / mm grating monochromator coupled with an EMI-9558 QB photomultiplier and a data acquisition system.

On the purpose to avoid some overlapping phenomena the intensity of a spectral line was considered to be the peak of the experimental spectral line profile.

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The evaluating of the relative line intensities was made by subtracting from the total experimental recorded intensity the light receiver noise and some possible noises coming from the overlapping continuous spectra.

We suppose, in agreement with some earlier published papers [3], [5], that the self-absorption phenomena are not relevant for these spectral systems in the experimental conditions, similar with ours.

3. Results and discussion

a) Band heads relative intensities behaviour in $N_2 + He$ gases

Due to the great variety of electron energies, we have had obtained an important number of helium spectral lines with upper energy levels of 23,01 – 23,70 eV and practical whole band heads of both system N^{2+} and N^{1-} placed in the spectral range 295,32 – 459,9 nm.

The relative intensities of some second positive system bands against the partial pressure of N_2 in the total pressure of the mixture $N_2 + He = 10$ torr are presented in (Fig.1). As we can see the relative intensities of the transitions arising from lower levels (0-0, 0-1) present a very slow increasing variation. The relative intensities for the transitions between the more elevated levels (0-2, 4-2) remain practically constant for the given partial pressure range. A slow intersection appears between the intensities corresponding to the transitions having the common lower level (0-2, 4-2). The behaviour of the relative intensities of the first negative band heads ($v'-v''$; 0-0; 0-1; 0-2; 3-2) shows a decreasing intensities with the partial pressure increasing especially for lower transitions (0-0, 0-1).

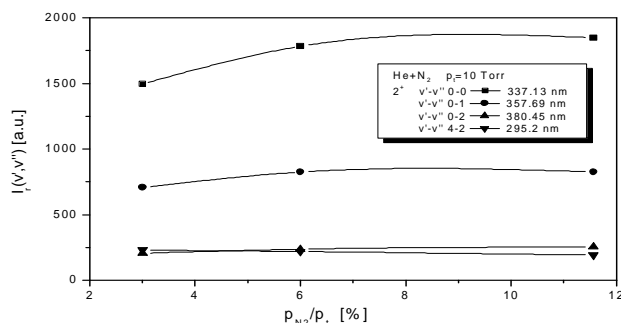


Fig. 1. The relative intensities of some N_2^{2+} system bands against the N_2 partial pressure in the $N_2 + He$ gas mixture.

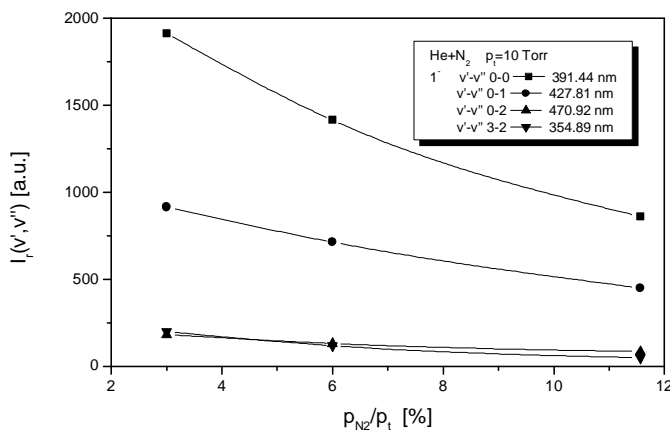


Fig. 2. The relative intensities of some N_2^{1-} system bands against the N_2 partial pressure in the $N_2 + He$ gas mixture.

For higher transitions (0-2, 3-2) the relative intensities remain practically constant, especially at higher partial pressure (Fig. 2).

Assuming the excitation and the ionisation of N_2 and N_2^+ systems as a result of the molecules collisions with the plasma electrons, by increasing the N_2 concentration in the $N_2 + He$ gas mixtures the concentration of the He is decreasing as well as the electronic temperature and consequently their ionization efficiency, as we know from the general properties of the electric gaseous phenomena [1].

This way the decreasing intensity of some 1^- system bands on the Fig. 2, is probably possible due to the decreasing of the ionic nitrogen molecular number with the increasing of the N_2 partial pressure in the $He + N_2$ mixture.

The decreasing of the He atomic spectral line relative intensities versus the partial N_2 increasing in $N_2 + He$ mixture gases gives us an idea about the electron temperature decreasing in the plasma source (Fig. 3), in the same manner we have had discussed before.

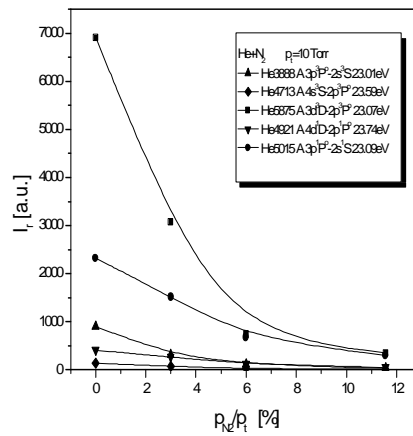


Fig. 3. The relative intensities of some He atomic spectral lines against the N_2 partial pressure in the $N_2 + He$ gas mixture.

b) The density of the upper excited vibrational level behaviour versus the partial pressure of the N_2 in the $N_2 + He$ gases mixture.

As we know the intensity of a band head is given by:

$$I_{v'v''} = DN_{v'}W_{v'v''}^4 R_e^2 (r_{v'v''}^-) q_{v'v''} \tag{1}$$

Where D is an instrumental factor, $W_{v'v''}$ is the quantum energy involved in the transition $v'v''$, R_e is the electronic transition moment, $q_{v'v''}$ is the Frank-Condon factor for the given transition, both these latter quantities being theoretically constant.

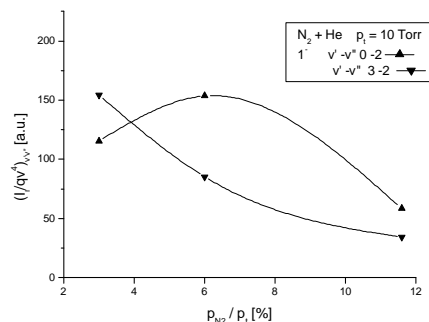


Fig. 4. The upper level of excited state populations of some vibrational levels belonging to the $N_2^+ 1^-$ system against the N_2 partial pressure in the $N_2 + He$ gas mixture.

From this equation is apparent that $(I / qv^4)_{v',v''}$ is a measure of the population of the v' level [3,4]. That is

$$(I / qv^4)_{v',v''} \sim N_{v'} \quad (2)$$

Concerning the upper level excited states population versus the partial N_2 in the $N_2 + He$ mixture for the N_2 first negative band, we observe a continuous decreasing of the $N_{v'=3}$ upper level, starting from an enough great value, an increase passing by a maximum of the upper level corresponding to the 0-2 transition (Fig. 4) (by $v'=0$ here we must understand the fundamental level of the upper excited electronic state which is not zero). In the first case we suppose the electrons with decreasing energy are not able to excite else the more elevated vibrational levels (e. g. $v' = 3$). In the second case, the nieder energy level ($v' = 0$) can also be excited with enough great probability, especially at small N_2 partial pressure values.

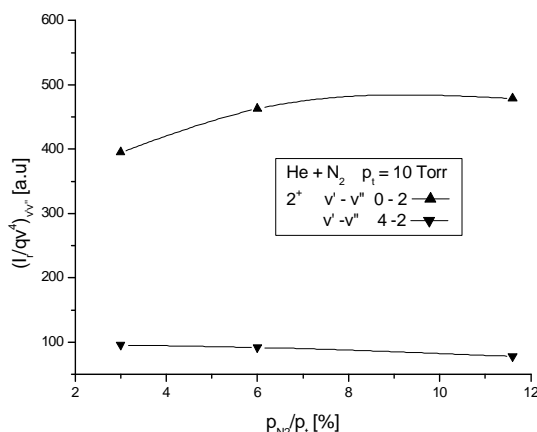


Fig. 5. The upper vibrational state populations corresponding to some vibrational transitions from the $N_2 2^+$ system against the N_2 partial pressure in the $N_2 + He$ gas mixture.

The intersection is produced at lower N_2 concentration in the $N_2 + He$ mixture. For the second positive system we have a very slow increase of the upper level of the transition $v' - v'' = 0-2$ and practically a constant value for $N_{v'=4}$ (Fig.5). That means the upper vibrational excited states of the N_2 molecule presents no variation with the N_2 increasing presence in the $N_2 + He$ mixture.

c) Some remarks about the ratio $I_{v',v'';i} / I_{v',v'';j}$ dependence of excitation conditions

From the equation (1) we got the following relationship for the ratio of two (spectral lines) band heads having a common upper vibrational level on an electronic molecular state.

$$\frac{I_{v',v'';i}}{I_{v',v'';j}} = \frac{W_{v',v'';i}^4 \operatorname{Re}^2(r_{v',v'';i}) q_{v',v'';i}}{W_{v',v'';j}^4 \operatorname{Re}^2(r_{v',v'';j}) q_{v',v'';j}} = \text{const.} \quad (3)$$

It results, as it is well known, this ratio is determined by molecular constants and is not depending on excitation conditions existing in the spectral sources. Nevertheless, it is of interest to outline some divergences from the theory discovered experimentally, in several conditions by several authors.

E. g. in [3] and [5] in several kinds of electric discharges in pure molecular nitrogen gas, some dependences of some band intensities ratio of the 2^+ system, having a common upper vibrational level from an electronic state on the electric current intensity (at a given gas pressure) went established.

A similar divergence from the theory regarding the intensity ratios $I_{v'v''i} / I_{v'v''j}$ for the N_2^+ first negative system against the partial pressure in a $N_2 + He$ gas mixture was published in the paper [4]. In this paper we have reported the partial pressure dependence p_{N_2} / p_t (%) of three band head relative ratios I_{00} / I_{01} , I_{00} / I_{02} and I_{01} / I_{02} belonging to the N_2 second positive system (Fig.6). As we can see these dependences are very slowly. More relevating is the I_{00} / I_{02} ratio dependence on this parameter.

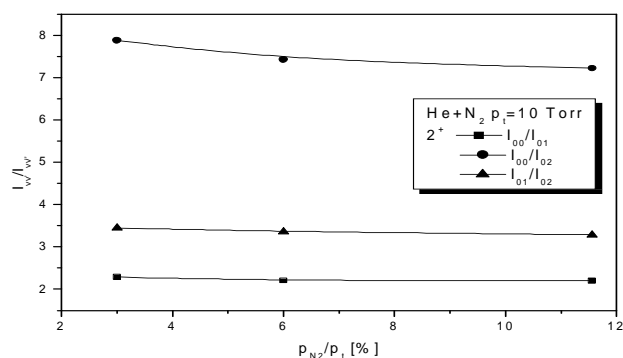


Fig. 6. Intensity ratios of some vibrational transitions having a common upper level from the N_2^+ 2⁺ system against the N_2 partial pressure in the $N_2 + He$ gas mixture.

We have had reported the same partial pressures ratios dependences p_{N_2} / p_t (%), this time for the band heads I_{00} / I_{01} , I_{00} / I_{02} and I_{01} / I_{02} ratios, belonging to the N_2^+ first negative (1^-) (Fig. 7). As we can see, no dependence on this parameter exists, for any ratios. That means, in this case, that no divergence from the theory can be remarked.

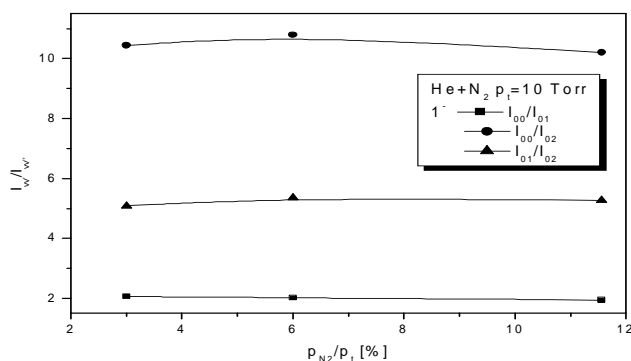


Fig. 7. The relative intensities of some band heads having a common upper level from the N_2^+ 1⁻ system against the N_2 partial pressure in the $N_2 + He$ gas mixture.

These complex molecular phenomena can't be easily explained. A more deep study must be done on this purpose. Of a great importance are some studies reported in [6] and [7] where are reconsidered the corresponding transition probabilities by re-evaluating the electronic transition probability and the Franck – Condon factors.

4. Conclusions

We have founded a very important behaviour of the relative band heads intensities of the N₂ first negative and second positive systems versus the partial N₂ concentrations in N₂ + He mixture.

We have established the conditions when the upper vibrational levels for the N₂ and N₂⁺ molecules are stimulated or destroyed, in the above mentioned mixtures.

A particular behaviour of second positive 2⁺ and first negative 1⁻ band heads ratios, having an upper common vibrational level versus the gas partial pressure p_{N₂} / p_t (%) were outlined.

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