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SOME REMARKS ON THE N_2 SECOND POSITIVE ($C\ ^3\Pi_u$ – $B\ ^1\Pi_g$) BAND HEADS RELATIVE INTENSITIES BEHAVIOUR IN A CYLINDRICAL HOLLOW CATHODE DISCHARGE

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Abstract. In a copper cylindrical cathode hollow effect discharge, in N_2 gas pressure of 1 – 10 Torr, at 200 – 400 volts and current intensities placed in the range 0 – 250 mA, we have had the good conditions for whole 2^+-band heads excitation. We have had established some irregularities behaviour in the band heads intensity ratios and the excited vibrational density number, against the current intensities.

These irregularities can be correlated with some discordance between the intensities calculated for individual systems, in pure equilibrium conditions, and the real conditions in our hollow cathode electric discharge plasma.

Key words: spectral sources, hollow cathode discharge, molecular spectroscopy.

1. INTRODUCTION

In this paper we operate on the specific potential and electric field distribution functions as well as on electrons energy distribution function, in such a discharge plasma existing two – three groups of electron energies in the range 1 – 50 eV [1 - 2], which allows us to excite a great variety of vibrational levels from two different electronic states of the diatomic molecule.

Here we will focus on the second positive 2^+ ($C\ ^3\Pi_u$ – $B\ ^3\Pi_g$) band heads (first time identified in the positive column of an electric discharge). For a proper use of the molecular nitrogen with its excited species who interferes as active factors in numerous reactions, like plasmochemical synthesis reactions, metallic surfaces nitriding [3], ionosphere reactions, lasers physics [4], etc., it is necessary to understand the mechanism of the electronic levels excitation and the band heads relative intensities behaviour in different excitation conditions as well as the vibrational levels population as function of some useful working parameters (as the discharge current intensity and the gas pressure).

The study of the 2^+ nitrogen system band heads relative intensities behaviour as function of the discharge current and gas pressure compared with the evolution of the upper vibrational levels density of the excited states represents the main purpose of this work. This study is as much important as some irregularities in such of behaviour types have already been described in some previous works [5 – 6].

2. THE EXPERIMENTAL SET – UP

The electric discharge tube from copper has a cylindrical geometry with a modular conception and it was presented in a previous paper [6].

This modular conception have been adopted for an easier variation of some parameters like the plasma column length. On the purpose to avoid the thermal influences on the electric and spectral measurements both the cathodes and anodes are water cooled during the electric discharge. Windows are made of quartz for spectral investigations in the visible and UV region. The discharge tube was connected to a standard vacuum system, which contains a diffusion pump that allows us to obtain a 10^{-5} – 10^{-6} torr vacuum. The working nitrogen pressures used are in the range of 1 –10 torr. The voltage obtained from a standard generator is between 200 – 400 V, and the discharge currents between 0 – 250 mA.

The spectrum was recorded with an experimental set-up consisting in a SPM-2 Zeiss 650 tr/mm grating monocromator coupled with an EMI – 9558 QB photomultiplier and a data acquisition system (for any further details see [7]).

The identification of the band heads was made by measuring the position within the spectrum of the band heads profiles maximum, and as a measure of the band heads relative intensities we have had also measured the intensity on the top of the profile, in order to avoid as much as possible the results distortion caused by any possible overlapping.

The identified band heads who will be studied in this paper are presented in the Tabel 1, in which we can see the molecular system affiliation, the electronic states between whom the transitions are taking place, the vibration levels involved and the corresponding band heads wavelengths. The caracteristics of these spectral lines can be seen [8].

For a precise comparison of the band heads relative intensities and of the evolution of the excited states densities on the vibration levels, we used four band heads groups with the same lower level and different upper levels. The lower levels mentioned in the Tabel 1 are: v'' = 1, v'' = 2, v'' = 3 and v'' = 8. The corresponding transitions for these levels groups are shown in the Figure 1.

Table 1
Band heads belonging to the N_2 2^+ system (C $^3\Pi_u$ – B $^3\Pi_g$)

Molecule	Spectral molecular system	*Electronic* transition	Vibrational transition v' → v"	λ [nm]
N_2	2^+	C → B	0 → 1	357, 69
N_2	2^+	C → B	2 → 1	313,60
N_2	2^+	C → B	3 → 1	296,20
N_2	2^+	C → B	0 → 2	380,49
N_2	2^+	C → B	1 → 2	353,67
N_2	2^+	C → B	3 → 2	311,67
N_2	2^+	C → B	4 → 2	295,32
N_2	2^+	C → B	0 → 3	405,94
N_2	2^+	C → B	1 → 3	375,54
N_2	2^+	C → B	2 → 3	350,05
N_2	2^+	C → B	4 → 3	310,40
N_2	2^+	C → B	3 → 8	441,67
N_2	2^+	C → B	4 → 8	409,48

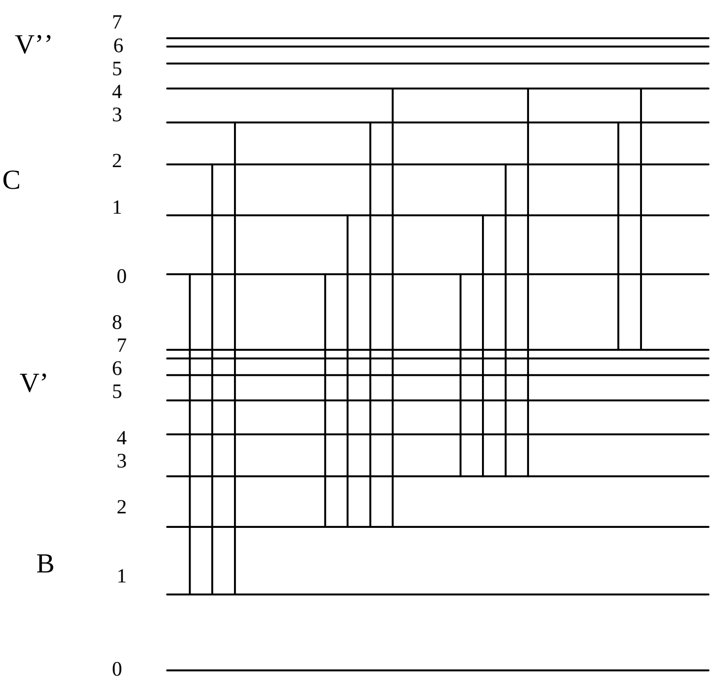

Fig. 1.

3. RESULTS AND DISCUSSIONS

At the base of the theoretical interpretations of the band heads relative intensities behavior and of the excited states density distributions on different vibration states, the following quantum relations were used:

$$I_{v'v''} = DN_{v'}W^4_{v'v''}R^2_e(\bar{r}_{v'v''})q_{v'v''} \qquad (1)$$

where D is an instrumental factor, $W_{v'v''}$ is the quantum energy involved in the transition v'- v", R_e (r) is the electronic transition moment, $q_{v'v''}$ is the Frank-Condon factor for the given transition, both these latter quantities being theoretically constant. From this equation is apparent that $(I / qv^4)_{v'v''}$ is a measure of the population of the v' level.

A. The band heads relative intensities and relative densities $N_{v'}$ as function of the discharge electric current

In the Figure 2 a, b, c, d corresponding to the same vibration quantum numbers of the lower states v" = 1, v" =2, v" = 3, v" = 8, we have the relative intensity distributions versus the discharge current (in mA) and in the Figure 2 a', b', c' d' we have the excited states population on different upper levels for the same groups of lower common levels (v" = 1, v" = 2, v" = 3, v" = 8).

From the representations of the band heads relative intensities and of the excited states population of the corresponding vibration upper levels as function of the discharge electric current, we remark, generally, a confirmation of the corresponding equilibrium distributions with the meaning that, the lines which results from the upper vibrational transition state on a common lower level are decreasing with increasing the corresponding vibrational quantum number. The same remarks we have for the upper levels populations. There are, however, some significant deviations from the classical distributions.

Examples:

In the case of the transitions on the common lower level v" = 1, the intensities of the three lines discussed here presents an intersection only at high values for the discharge currents, of about 200 mA, while the populations, only those of the levels v" = 2 and v" = 3 have an intersection the same at high currents of 150 mA.

In the case of the transitions on the same lower level v" = 2, the intensity for the transition v' = 4 – v" = 2 presents lower values than the others transitions only at lower currents (~ 20 mA), while for higher

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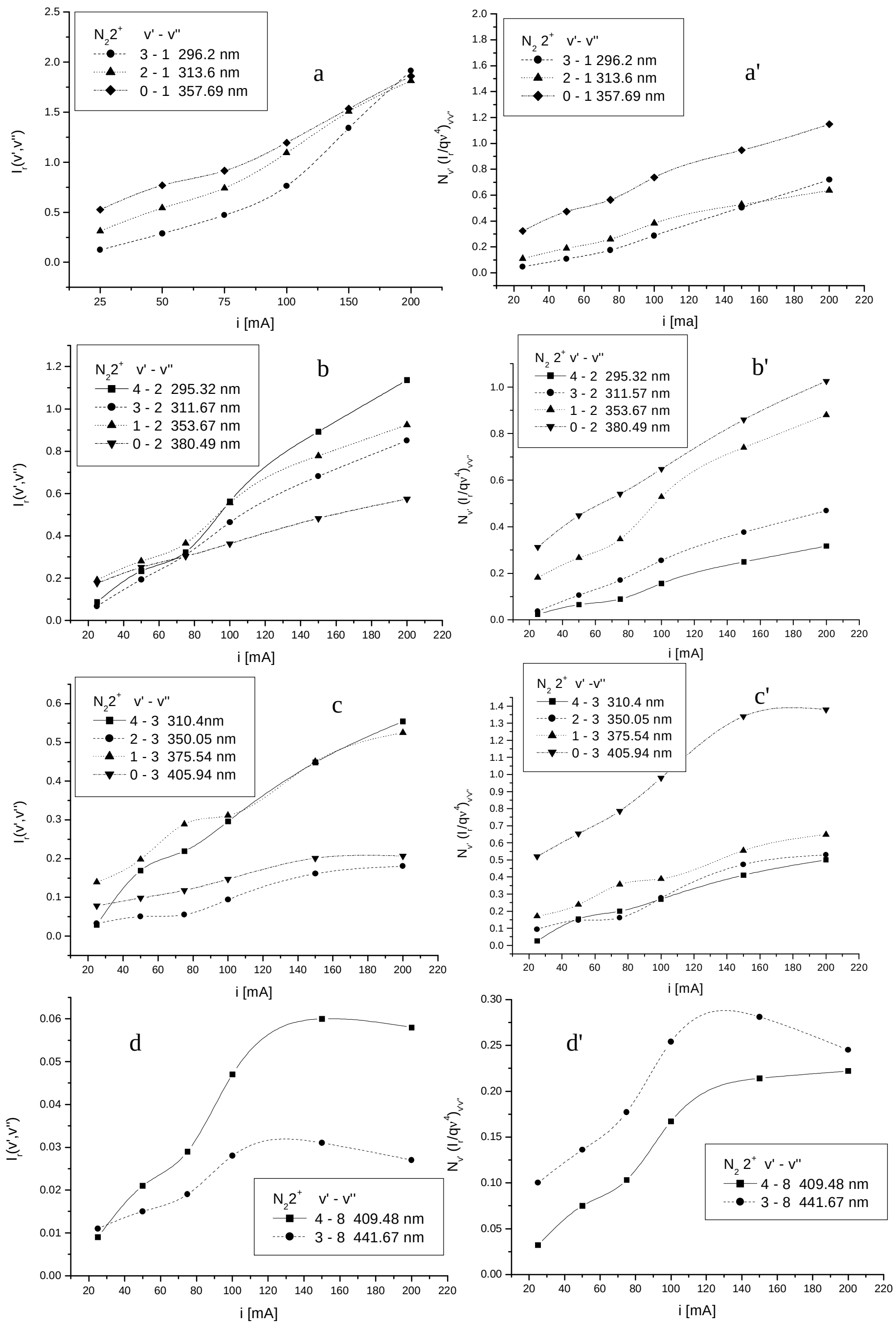

a
N22+ v' - v''
3 - 1 296.2 nm
2 - 1 313.6 nm
0 - 1 357.69 nm
Ir(v',v'')
i [mA]
a'
N2 2+ v'- v''
3 - 1 296.2 nm
2 - 1 313.6 nm
0 - 1 357.69 nm
Nv' (Ir/qv4)v'v''
i [ma]
b
N22+ v' - v''
4 - 2 295.32 nm
3 - 2 311.67 nm
1 - 2 353.67 nm
0 - 2 380.49 nm
Ir(v',v'')
i [mA]
b'
N2 2+ v' - v''
4 - 2 295.32 nm
3 - 2 311.57 nm
1 - 2 353.67 nm
0 - 2 380.49 nm
Nv' (Ir/qv4)v'v''
i [mA]
c
N22+ v' - v''
4 - 3 310.4nm
2 - 3 350.05 nm
1 - 3 375.54 nm
0 - 3 405.94 nm
Ir(v',v'')
i [mA]
c'
N2 2+ v' -v''
4 - 3 310.4 nm
2 - 3 350.05 nm
1 - 3 375.54 nm
0 - 3 405.94 nm
Nv' (Ir/qv4)v'v''
i [mA]
d
N22+ v' - v''
4 - 8 409.48 nm
3 - 8 441.67 nm
Ir(v',v'')
i [mA]
d'
N2 2+ v' - v''
4 - 8 409.48 nm
3 - 8 441.67 nm
Nv' (Ir/qv4)v'v''
i [mA]

Fig.2.

currents (~ 200 mA) it becomes higher than all other transitions. Regarding the populations, intersections are observed only for v" = 4 and v" = 3 populations. We mentioned that a similar behavior for the level with v' = 4 have been found in a previous work, in almost the same experimental conditions, when this level interferes with levels 0 and 1 [6].

In the case of the transitions on the same lower level v" = 3, a complete different behavior of the intensities versus the current it has again the transition with the upper level v' = 4, who presents intensity values (for the entire range of the current variation) that leads to intersections with all the other transition intensities. The evolution for the upper state population (with v' = 4) shows an intersection only with the state v' = 3 population, which completes the information in this area (more intersections with lower v' levels were observed).

In the case of the transitions on the same lower level v" = 8, the intensities are crossing in reversed order only at small currents (~ 20 mA), while the densities follows their normal behavior.

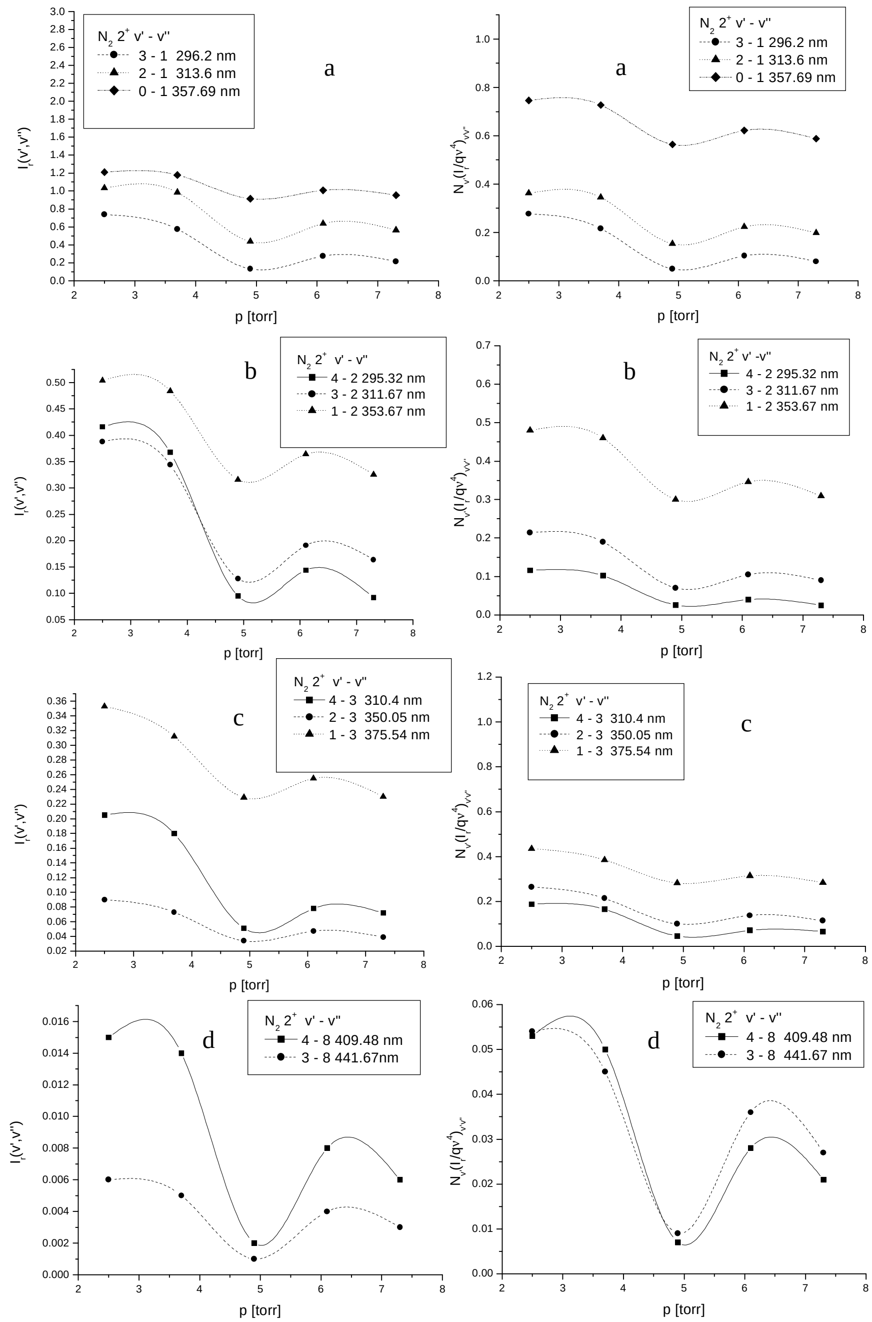
B. The band heads relative intensities and relative densities $N_{v'}$ as function of the N_2 gas pressure

Regarding the study of the transition intensities evolution as function of the gas pressure (Figure 3 a, b, c, d) and of the excited states population versus the same parameter (Figure 3 a', b', c', d') we can make the following observations:

In the case of the common lower level with v" = 1, both the intensities and the populations confirms the classical distributions rules.

In the case of the common lower level with v" = 2, the intensities evolution presents a small intersection only for the transitions 4 – 2 and 3 – 2 at small pressure values (~ 4 torr), at higher pressure the related distribution is normal. The excited states population versus the gas pressure presents evolutions according with the classical distributions. In the case of the transitions to the common lower level with v" = 3, the intensities presents an inversion only for the transitions 4 – 3 and 2 – 3, while the excited states populations presents a normal evolution, decreasing with the gas pressure.

Finally, in the case of the transitions to the common lower level with v" = 8, the intensities evolution versus the gas pressure presents a minimum value around p = 5 torr, and an unusual inversion between the transitions v' = 4 – v" = 8 and v' = 3 – v" = 8, while the population evolution presents an inversion only for pressure below 4.5 torr.



a
$I_r(v',v'')$
p [torr]
N_2 2^+ v' - v''
3 - 1 296.2 nm
2 - 1 313.6 nm
0 - 1 357.69 nm
a
$N_{v'}(I_r/qv^4)_{v'v''}$
p [torr]
N_2 2^+ v' - v''
3 - 1 296.2 nm
2 - 1 313.6 nm
0 - 1 357.69 nm
b
$I_r(v',v'')$
p [torr]
N_2 2^+ v' - v''
4 - 2 295.32 nm
3 - 2 311.67 nm
1 - 2 353.67 nm
b
$N_{v'}(I_r/qv^4)_{v'v''}$
p [torr]
N_2 2^+ v' -v''
4 - 2 295.32 nm
3 - 2 311.67 nm
1 - 2 353.67 nm
c
$I_r(v',v'')$
p [torr]
N_2 2^+ v' - v''
4 - 3 310.4 nm
2 - 3 350.05 nm
1 - 3 375.54 nm
c
$N_{v'}(I_r/qv^4)_{v'v''}$
p [torr]
N_2 2^+ v' - v''
4 - 3 310.4 nm
2 - 3 350.05 nm
1 - 3 375.54 nm
d
$I_r(v',v'')$
p [torr]
N_2 2^+ v' - v''
4 - 8 409.48 nm
3 - 8 441.67nm
d
$N_{v'}(I_r/qv^4)_{v'v''}$
p [torr]
N_2 2^+ v' - v''
4 - 8 409.48 nm
3 - 8 441.67nm

Fig.3

Linear variations of the intensities and excited states populations through wide ranges of currents, means that we have an excitation of the upper vibration levels mainly by direct electronic collisions. Nonlinear variation of the radiation intensities and of the vibration states densities with the gas pressure, especially at higher pressure (over 5 torr), suggest that, in this case, the vibration levels excitation processes are no longer produced mainly by electronic collisions. In this case, complex molecular interactions processes appears which affects directly the vibration levels.

4. CONCLUSIONS

In the cylindrical hollow cathode electric discharges, in molecular nitrogen, at low pressures, the upper vibration levels excitation is produced mainly by electronic collisions. At higher pressures, above 5 torr, some very important molecular processes appears, which affects the particles energy functions distributions and consequently the vibration levels excitation. In the HCC electric discharge, appears some specific conditions for population inversion, for some upper vibration levels, like v' = 3 and v' = 4.

REFERENCES

1. E. Badarau, I. I. Popescu, “Gaze ionizate. Descarcari electrice in gaze”, *Ed. Tehnica* (1965).
2. E. Badarau, I. I. Popescu, I. Iova, *Rev. d. Phys.*, **5**, 287 (1960).
3. L. Deshayes, M. Charbonnier, N. S. Prohash, F. Gaillard, M. Romand, *Surface and interface analysis,* **21**, pp. 711-717 (1994).
4. C. K. N. Patel, P. K. Tien, J. N. Mc Fee, *Appl. Phys. Lett.,* **7**, 290 (1965).
5. D. C. Tyte, *Proc. Phys. Soc.,* **80**, pp.1364 (1962).
6. I. Iova, M. Bazavan, Fl. Iova, *Rom. Rep. Phys.,* **55**, No. 4 (2003).
7. I. Iova, M Bazavan, Gh. Ilie, C. Biloiu, *Rom. Rep. Phys.,* **54**, No. 1-2, pp. 135-147 (2002).
8. A. Lofthus, P. H. Krupeni, *Phys. Chem. Ref. Data,* **5**, 113 (1977).