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SPECIFIC EXCITATION OF SOME HEAD BANDS OF N_2 AND N_2^+ MOLECULES IN A CYLINDRICAL HOLLOW CATHODE ELECTRIC DISCHARGE (HCED)

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Abstract. The purpose of this paper is to use the nonmaxwellisation of electron's energy distribution produced in the molecular gas of an HCED, to explain a specific excitation of neutral N_2 molecule [2^+ system] or of the ionical nitrogen molecule [1^- system], in pure N_2 gas. The head bands relative intensity distribution give as a very important information about the excitation processes localization and electron temperature distribution evaluation.

We have established the existence of the direct electron-molecule collision excitation of the upper neutral or ionical molecular levels and also the fact that the intensity distribution of some band heads is not the same with the upper vibrational levels of the neutral molecule density ($N_{v'}=4$) distribution.

Keywords: hollow cathode electric discharge, diatomic molecular spectroscopy, electronic excitation.

1. INTRODUCTION

As we can se from the potential curves involved in the transitions for second positive ($C\ ^3\Pi_u - a\ ^1\Pi_g$) system and for the first negative one ($B\ ^2\Sigma_u^+$ - $X\ ^2\Sigma_g^+$) the electronic and vibrational levels are placed approximately on the ranges (9-11.5) eV and (15-22) eV, respectively (Fig. 1.) [1]. For a simultaneously excitation of this both systems we have used a nonmaxwellized electrons energy distribution produced in the molecular gas of an hollow cathode electric discharge (HCED), where we get at lest two groups of electron energy [2].

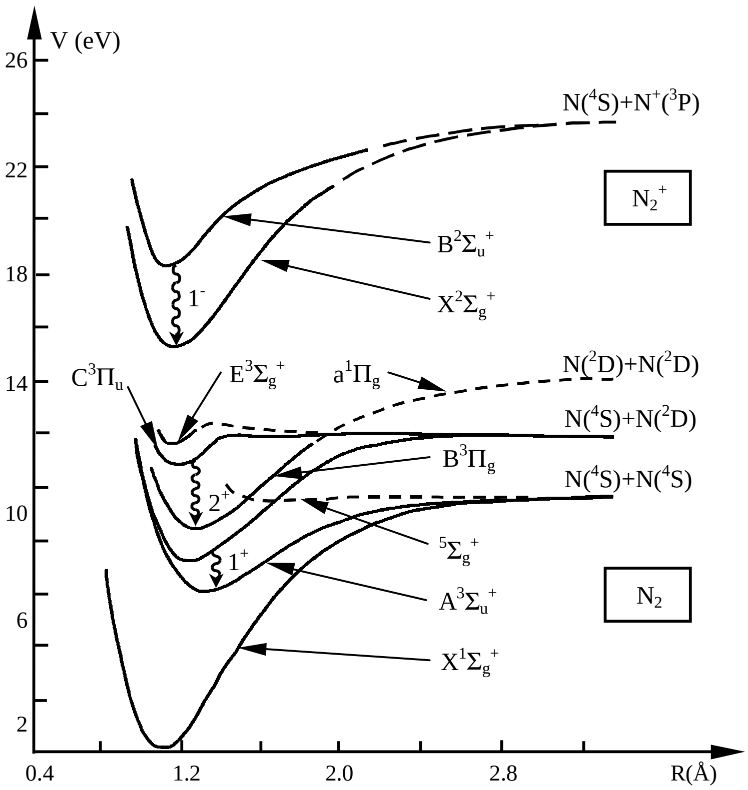

Fig. 1. - Potential curves of the neutral and ionized nitrogen molecule

2. BASICALLY RELATIONSHIP FOR DIATOMIC MOLECULE SPECTRA

This paper describes an experimental examination of the head bands intensity variation, when the conditions of excitation are changed, with special references to the current intensities.

It is the reason we retain, from the general theory of molecular intensities and their interpretation, the basic equation relating the intensity $I_{v'v''}$ of the $v'v''$ band of system to the population $N_{v'}$ in the excited state. So we have:

$$I_{v'v''} = DN_{v'}E^4_{v'v''}R^2_e\left(\overline{r_{v'v''}}\right)q_{v'v''} \qquad (1)$$

where

D is an instrumental constant;

$E_{v'v''}=h\nu_{v'v''}$ is the quantum of energy involved in the transition $v'v''$;

$R_e(r)$ is the electronic transition moment;

$q_{v'v''}$ is the Franck-Condon factor for the transition, both these latter quantities are theoretically constant.

From the above it is also clear, if the theory is correct, $I_{v'v_1''} / I_{v'v_2''}$ must be constant for all conditions. The same from (1) it is apparent that $(I/qv^4)_{v'v''}$ is a measure of the population of the *v'* level.

3. EXPERIMENTAL

The excitations of the nitrogen molecular systems were made in the negative glow plasma produced in a water cooled cylindrical HCED, presented in a earlier published paper [2].

In order to avoid the thermal influences on the electric and spectral measurements the copper cathodes and anodes were water-cooled.

The cylindrical cavity has an inner diameter of *6 mm* and a length of *30 mm*.

The electric discharge tube was connected to a vacuum pump. The pressure of the spectral pure N_2 was varied in the range of *0.5-10 Torr*.

In the experimental set-up we had a *SPM-2 Zeiss 650 tr/mm* grating monochromator coupled with a *EMI-9558QB* photomultiplier and a *SEFRAM GRAPHYSPOT II* recorder.

The voltage was varied in the range *200-400 Volts* and the electric current intensity in the range *0-250 mA*.

4. RESULTS AND DISCUSSIONS

The Volt-Ampers characteristics of the electric discharge in pure N_2, at two different pressures values are represented on the figure 2. These two curves are placed very close to each other. They presents a small discrepancy only at higher currents (over *150 mA*).

We must to outline we are now in the abnormal glow discharge on the

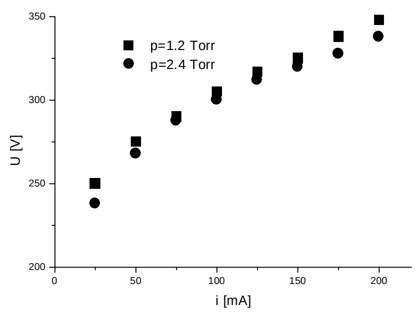

Fig.2.

general Volt-Amper characteristic of an electric discharge. This means we can have an important number of energetic electrons, even at relatively high electric currents.

In order to avoid the possible band overlap the head bands positions were measured by the peak-height method.

On the tables I and II are presented a number of the remarkable band heads from the second positive and first negative systems of the nitrogen molecule respectively and their characteristic parameters mentioned in A.Lofthus and P.H.Krupenie's tables [1].

On the figure 3(a) and 3(b) are represented the relative intensity distribution of the 2^+ system band heads: *λ 380.5 nm (0-2), λ 375.5 nm (1-3), λ 371.05 nm (2-4), λ 441.7 nm (3-8), λ 409.5 nm (4-8)* and of the 1^- systemband heads: *λ 391.6 nm (0-0), λ 423.6 nm (1-2), λ 459.9 nm (2-4), λ 455.4 nm (3-5), λ 451.5 nm (4-6)* for two no very different pressure (*p=1.2 Torr* and *p=2.4 Torr*) versus the discharge electric current intensity, respectively.

Concerning the N_2 band heads behaviour we ca remark a more and more linear dependence of electric currents as the upper vibrational level is increasing.

Concerning the N_2^+ band heads (1^- system), practically all the head bands relative intensities are linearly depending on current intensities, except *λ 391.6 nm (0-0)* which a resonant line being can support a significantly absorption phenomenon.The population of the upper vibrational states of the molecule $N_{v'}$ in plasma molecular processes and in plasma sources too is of the great importance.

We remember, from the first mathematical relationship we have outlined the ratio $(I/q\nu^4)_{v'v''}$ is a measure of the density of upper excited molecular states ($N_{v'}$). By using Franck-Condon factor for the transitions from Alf Lofthus and Paul H. Krupenie's tables [1] we have had calculated $N_{v'}$ for three levels belonging to the N_2 second positive (*v'=0, v'=1, v'=4*), for three levels belonging to the N_2^+ first negative system (*v'=2, v'=3, v'=4*) as electric current intensities, results which are presented in the fig. 4 and fig. 5 respectively.

As we can see all the levels of the 1^- system and the first two of the second positive system are in good agreement with thermodinamical equilibrium laws: the populations are decreasing with vibrational quantum number is increasing. Exception is only $N_{v'}$ with *v'=4* from the second positive system, which respect the above equilibrium law at the lower currents only. At higher currents this population, abnormaly, becomes greater han for lower levels. This may be due to a fort perturbation between interacting vibration levels, a greater value of this upper level life time or to some wrong data from the mentioned references.

As we have had mentioned in the first part, if the relationship resulting from (1) are correct, then $I_{v'v_1''} / I_{v'v_2''}$ must remain a constant for all conditions. We have had calculated these ratios for two couples of transitions

TABLE I- Band heads belonging to the N_2 2^+ system ($C\ ^3\Pi_u - B\ ^3\Pi_g$), and their characteristic parameters

Molecule	Spectral molecular system	Electronic transition	Vibrational transition v'→v''	λ [nm]	$q_{v'v''}$ factor Franck-Condon	Absolute transition probabilities [10^8 s^{-1}]
N_2	2^+	C → B	3→5	367.19	0.04236	2.19
N_2	2^+	C → B	2→4	371.05	0.1246	3.80
N_2	2^+	C → B	1→3	375.5	0.1973	4.62
N_2	2^+	C → B	0→2	380.5	0.1661	3.34
N_2	2^+	C → B	2→5	394.3	0.1431	2.77
N_2	2^+	C → B	1→4	399.8	0.1306	2.12
N_2	2^+	C → B	0→3	405.94	0.06692	0.96
N_2	2^+	C → B	4→8	409.5	0.09428	1.73
N_2	2^+	C → B	3→8	441.7	0.08058	0.74

TABLE II- Band heads belonging to the N_2^+ 1^- system ($B\ \Sigma_u^+ - X\ \Sigma_g^+$), and their characteristic parameters

Molecule	Spectral molecular system	Electronic transition	Vibrational transition v'→v''	λ [nm]	$q_{v'v''}$ factor Franck-Condon	Absolute transition probabilities [10^6 s^{-1}]
N_2^+	1^-	B → X	0→0	391.4	0.6481	9.64
N_2^+	1^-	B → X	1→2	423.6	0.2889	3.87
N_2^+	1^-	B → X	4→6	451.5	0.1550	-
N_2^+	1^-	B → X	3→5	455.4	0.1720	2.00
N_2^+	1^-	B → X	2→4	459.9	0.1699	1.94

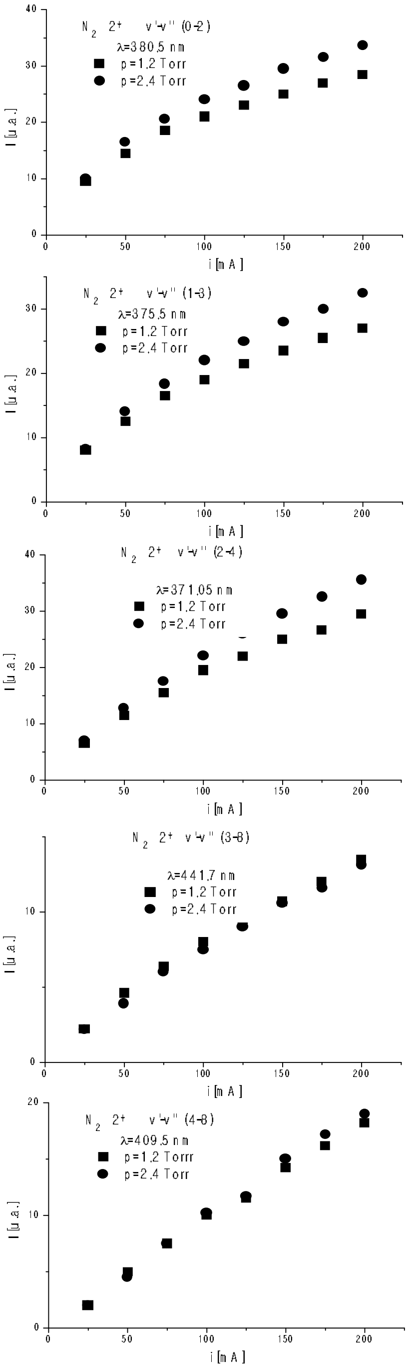
N2 2+ v'-v'' (0-2)
λ=380.5 nm
p=1.2 Torr
p=2.4 Torr
N2 2+ v'-v'' (1-3)
λ=375.5 nm
p=1.2 Torr
p=2.4 Torr
N2 2+ v'-v'' (2-4)
λ=371.05 nm
p=1.2 Torr
p=2.4 Torr
N2 2+ v'-v'' (3-8)
λ=441.7 nm
p=1.2 Torr
p=2.4 Torr
N2 2+ v'-v'' (4-8)
λ=409.5 nm
p=1.2 Torrr
p=2.4 Torr
I [u.a.]
i [mA]

Fig. 3a

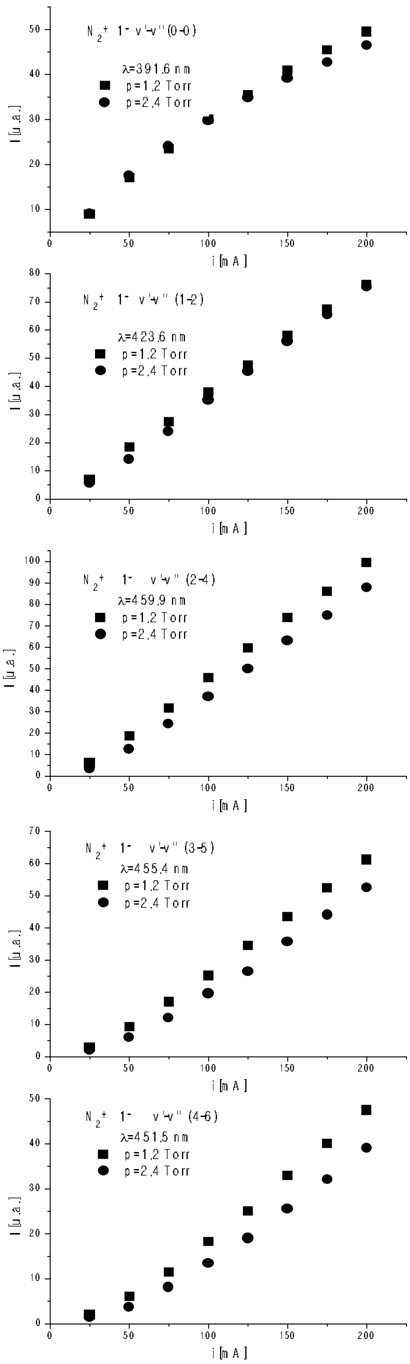
N2+ 1- v'-v'' (0-0)
λ=391.6 nm
p=1.2 Torr
p=2.4 Torr
N2+ 1- v'-v'' (1-2)
λ=423.6 nm
p=1.2 Torr
p=2.4 Torr
N2+ 1- v'-v'' (2-4)
λ=459.9 nm
p=1.2 Torr
p=2.4 Torr
N2+ 1- v'-v'' (3-5)
λ=455.4 nm
p=1.2 Torr
p=2.4 Torr
N2+ 1- v'-v'' (4-6)
λ=451.5 nm
p=1.2 Torr
p=2.4 Torr
I [u.a.]
i [mA]

Fig.3b

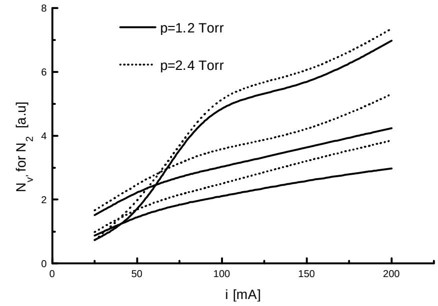

Fig.4.

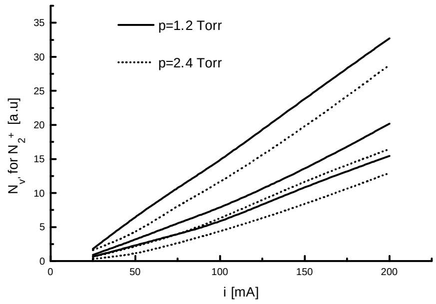

Fig.5.

belonging to the second positive *v'=1-v''=4/v'=1-v''=3* and *v'=2-v''=5/ v'=2-v''=4*, in function of electric current intensities and the results are reported in the table III.

TABLE III- The intensities ratios for various currents of two pairs of head bands belonging to the 2^+ system of nitrogen molecule, heaving common upper states

Bands $v'-v_1'' / v'-v_2''$	Ratio of q values	Observed ratios for the following currents [mA]				
		50	75	100	150	200
1-4 / 1-3	0.662	1.78	2.17	2.35	2.50	2.74
2-5 / 2-4	1.148	1.36	1.43	1.44	1.51	1.50

As we can see these variations of the ratio of intensity of two bands from a common upper level especially at lower currents , are quite contrary of the theoretical expectations, and indicate that the present theory is inadequate under certain conditions. The similar observations, in other electric discharges spectral sources, were made also in some earlier published papers [4].

5. CONCLUSION

A large variety of the electron energy distribution in the HCED gives us the possibility to realize an adequate excitation of the vibrational states in the 2^+ an 1^- systems of the nitrogen molecule. The observed variation in the ratio of intensities of two bands from a common upper state is completely contrary to theoretical expectations and is most marked at low current densities. A special behaviour of the *v'=4* upper vibrational level population gives….as a test about a difference which sometimes exist between intensity and excited levels

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