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THE INFLUENCE OF THE METASTABLE STATE $A^3\Sigma_u^+$ IN THE EXCITATION MECHANISM OF MOLECULAR NITROGEN FOR NON EQUILIBRIUM PLASMA. CASE OF LOW CURRENT ARC IN EXTINCTION.

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Abstract :

In this paper, the influence of the metastable state $A^3\Sigma_u^+$ of N_2 on the excitation mechanism is experimentally and theoretically solved. Experimental part is based on study of the emitted light from the cathodic region during the spontaneous extinction of a low current electric arc. A theoretical approach is proposed on the basis of Franck-Condon factors calculations. Electron impact cross sections for transitions $A^3\Sigma_u^+ \rightarrow C^3\Pi_u$ and $A^3\Sigma_u^+ \rightarrow B^2\Sigma_u^+$ are unknown.

Taking into account a partial excitation starting from the metastable state $A^3\Sigma_u^+$, the use of the Franck-Condon factors enables us to compute spectra of the second positive system (2s+) from transition $C^3\Pi_u \rightarrow B^2\Sigma_u^+$ and the first negative system (1s-) from transition $B^2\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ of nitrogen N_2. The calculated spectrum is in agreement with an experimental one.

Keywords :

Electrical arc, Plasma, Metastable state, Molecular nitrogen, Spectroscopy.

Résumé :

L'arc électrique à bas courant présente des instabilités pouvant aboutir à son extinction. Les fluctuations de la tension ainsi que les phénomènes lumineux impulsionnels reflètent ces instabilités internes. Dans ce papier, le rôle de l'état métastable $A^3\Sigma_u^+$ de N_2 dans les mécanismes d'excitation est élucidé expérimentalement par l'étude de la lumière émise par la région cathodique au moment de l'extinction. Une approche théorique est utilisée sous forme de calcul des facteurs de Franck-Condon. Le résultat du calcul confirme les interprétations des observations expérimentales.

1. Introduction :

The cathodic region plays a major role in the self-sustaining arc discharge. The low DC current arc between metallic electrodes exhibits internal instability, leading to complete extinction.

The electrical study of this phenomenon in the air at atmospheric pressure [1], [2] shows that these instabilities result in voltage fluctuations and sharp rises of the voltage, due to the sharp decrease of the current.

This electrical phenomena are correlated with an intense and brief emission of NII, OII, AgII and N_2, and a decrease of the emission of AgI coming from the region close to the silver cathode.

A previous spectroscopic study [1], [3], [4] allowed us to show the excitation mechanisms of the different species. We proposed a detailed analysis of the resulting spectra, namely the intensity of the heads of 2s+ and 1s- of the N_2 molecular bands. We assume that, at the time of the extinction, two groups of electrons exist in the plasma : a group of electrons with thermal energy and a group of fast electrons (> 40 eV) emitted by the cathode and accelerated in the cathode sheath. This last group is involved in the intense light emission from the region close to the cathode.

Here, our attention is focused on the results concerning the N_2 and N_2^+ emission, in particular, the intensity of the 2s+ and 1s- band's heads.

The experimental data are presented using time resolved spectroscopy as an investigation mean. An abnormal distribution of the intensity of the molecular band of the 2s+ system of N_2 is observed in the light from the cathodic region.

This suggests that a partial electron excitation of the electronic level $C^3\Pi_u$ is possible, starting from the metastable level $A^3\Sigma_u^+$. At this time, the cross sections for this electron impact transition are unknown. Similarly, the Franck-Condon factors are omitted in the tables, since this transition is non radiative. The cross sections values cannot easily be theoretically evaluated, but the Franck-Condon factors can be accessed by computation following the method given by Nicholls [5].

2. Experimental set-up :

A DC high voltage supply allows the re-ignition of the arc by thermal breakdown after an extinction. The circuit was described in previous works [1], [2], [3] allows us to record numerous observations of extinctions and subsequent re-ignitions without external intervention.

To be analysed, the light emitted by a thin part of the arc located at a known distance from the cathode, is focused by a concave mirror on the entrance slit of the monochromator followed by a photomultiplier. The trigger of the sorting vs. time of the light pulses is taken from the arc voltage using the fast rising slope dv/dt of the long pulses (Figure1).The recording apparatus was described in a previous studies [1], [2], [3].

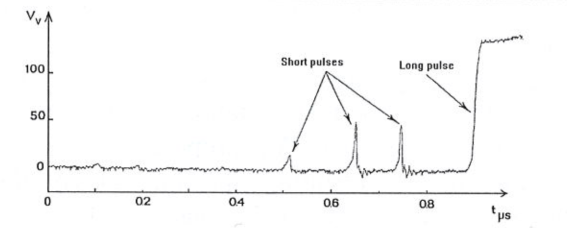

Figure 1: Arc voltage variation showing short voltage pulses preceding the total extinction of the arc, referenced as a long pulse.

3. Experimental results and discussion :

We established the histograms of the light emitted in the cathodic region for Ag electrodes from 210 nm to 510 nm by steps of 0.5 nm.

An interesting phenomenon appears as a short and intense light emission coming from the region close to the cathode at the instant of extinction (channel 80). The detailed results of this phenomena are presented in our previous works [1], [3].

For molecular nitrogen N_2, the typical shape of the histograms obtained is displayed on fig.2.

The stationary spectrum [1], [6] shows that the molecular bands of the second positive system 2s+ are permanently excited. In fact, if we substract from the histogram of N_2 ($\lambda = 295.3$ nm for example), the histogram of very near continuum (λ =299.0 nm), the result, on fig. 3, shows the existence of an emission of nitrogen molecule before the extinction of the arc. The light pulse observed at the instant of extinction corresponds to a reinforcement of the emission of N_2.

At the moment of extinction (channel 80), the recorded spectrum [1], [3] shows that the intensity of band's heads is disturbed with respect to the structure of the molecular spectrum when the population of the excited states $C^3\Pi_u$ and $B^2\Sigma_u^+$ are done starting from the fundamental state $X^1\Sigma_g^+$ [7].

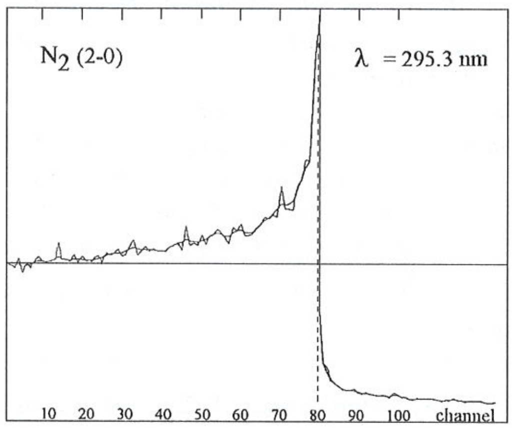

Figure 2: Evolution of light intensity coming from the cathode region, corresponding to λ =295.3 nm, N_2 .

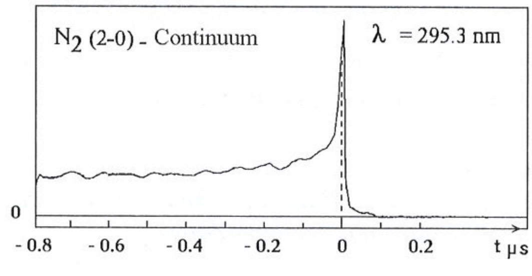

Figure 3: Evolution of light intensity after substraction of the continuum : λ =295.3 nm, N_2 and λ =299.0 nm, continuum.

The first electronic excited state $A^3\Sigma_u^+$ of N_2 is a metastable state, for which the life span for the isolated molecule is about 12-13 s [8], [9]. The second metastable state is the excited state $B^2\Sigma_u^+$ for which the life span for the isolated molecule is about 2 to 8 □s [8], [9]. However, at atmospheric pressure, we obtain a quenching effect of this state by collisions with the gas species [10]. The life span of such state becomes of the order of one nanosecond. On the contrary, the metastable state $A^3\Sigma_u^+$ is more stable at atmospheric pressure (life span of the order of a few milliseconds)[11].

It results that the radiating levels $C^3\Pi_u$ and $B^2\Sigma_u^+$ are probably populated in cascade using the metastable level $A^3\Sigma_u^+$, which requires electrons of lower energy.

4. Calculation results and simulated spectra :

The collisional cross sections of transitions $A^3\Sigma_u^+ \rightarrow C^3\Pi_u$ and $A^3\Sigma_u^+ \rightarrow B^2\Sigma_u^+$ being unknown, as an approximation, we can use the Franck-Condon factors for these transitions. We used the method developed by Nicholls [5] for the computation of this Franck-Condon factors. To our knowledge, this calculation was never done, because of the non radiating character of this transitions.

The computed values of the Franck-Condon factors are given in tables 1 and 2.

The computed factors are then introduced in the simulation code for the second positive system of N_2 already made by Hartmann and Johnson [12], further used for spectra simulations [13-16]. Simulation of the first negative system of N_2 was made later.

The present simulated spectra are obtained assuming 5000 K for the rotation and vibration temperatures. The entrance and exit slits of the assumed monochromator are of 0.1 and 0.5 nm equivalent width respectively. The displacement is by 0.5 nm steps.

We show the simulated spectra of the second positive system (2s+) of N_2 on figs. 4a, 4b, respectively, assuming a 100% production either from ground or metastable states. On figures 4c and 4d, are shown the same simulated spectra for the first negative system (1s-) of N_2.

If we assume for the $C^3\Pi_u$ state, whose populating is starting, 30% from fundamental and 70% from metastable states $A^3\Sigma_u^+$ and for the $B^2\Sigma_u^+$ state (75% and 25% respectively), we finally obtain a spectrum formed by 60% of $C^3\Pi_u$ and 40% of $B^2\Sigma_u^+$ as shown on fig. 5a vs. fig. 5b.

Note that this result agrees with our interpretation of the experimental results.

5. Conclusion :

During the transient phenomena which happen just at the extinction of a low current arc in air, the nitrogen molecular spectra is strongly anomalous, compared to that of the steady arc discharge.

The hypothesis of a cascade excitation mechanism using the metastable level $A^3\Sigma_u^+$ and the computation of the related Franck-Condon factors, for the populations of the excited states $C^3\Pi_u$ and $B^2\Sigma_u^+$ are in agreement with the observed spectrum at the instant of extinction.

The influence of the excitation of the $C^3\Pi_u$ and $B^2\Sigma_u^+$ states starting from the $A^3\Sigma_u^+$ metastable state seems clear evident. Of course, for a thermodynamically equilibrium state plasma, this influence is negligible, but for cold plasmas or arcs in extinction, which are of interest here, this becomes important. The electrons present at the spontaneous extinction of a low current arc have an evaluated kinetic energy higher than 40 eV, far from thermal equilibrium [1], [3].

v"/v'	0	1	2	3	4
0	.023	.110	.252	.363	.311
1	.071	.181	.148	.013	.068
2	.120	.139	.008	.085	.170
3	.148	.056	.028	.132	.009
4	.151	.006	.088	.040	.050
5	.134	.004	.090	.001	.106
6	.108	.031	.049	.041	.054
7	.081	.059	.011	.079	.003
8	.058	.076	-	.072	.014
9	.039	.079	.013	.039	.051
10	.026	.072	.034	.010	.068
11	.017	.060	.051	-	.055
12	.011	.047	.061	.008	.028
13	.007	.035	.062	.025	.007
14	.004	.026	.057	.041	-
15	.002	.018	.049	.052	.005

Table 1: The computed values of the Franck-Condon factors for $A^3\Sigma_u^+(v'') \rightarrow C^3\Pi_u(v')$.

v"/v'	0	1	2	3	4	5	6	7	8	9	10	11
0	-	.002	.013	.05	.134	.235	.341	.347	.283	.177	.082	.030
1	.001	.012	.052	.0135	.221	.186	.071	-	.091	.248	.295	.227
2	.003	.033	.104	.175	.143	.022	.025	.139	.135	.018	.040	.214
3	.007	.063	.142	.137	.029	.020	.122	.074	.001	.102	.133	.017
4	.014	.096	.144	.061	.003	.089	.073	.001	.091	.077	.001	.110
5	.024	.121	.111	.008	.049	.085	.003	.062	.070	.001	.092	.053
6	.036	.123	.064	.004	.085	.029	.024	.077	.002	.067	.047	.013
7	.048	.126	.023	.031	.074	-	.067	.024	.029	.064	.001	.081
8	.060	.107	.002	.059	.036	.018	.062	-	.065	.007	.050	.033
9	.070	.080	.002	.069	.006	.048	.024	.027	.042	.011	.056	.001
10	.077	.052	.017	.058	.002	.056	.001	.052	.005	.046	.013	.039
11	.081	.028	.035	.036	.018	.040	.009	.044	.005	.048	.002	.051
12	.082	.011	.050	.015	.037	.017	.031	.018	.028	.019	.028	.019
13	.081	.002	.057	.002	.049	.002	.044	.001	.042	-	.042	-
14	.078	-	.055	.001	.047	.002	.040	.004	.034	.008	.029	.014
15	.072	.004	.047	.007	.035	.012	.024	.019	.015	.026	.007	.033

Table 2 : The computed values of the Franck-Condon factors for $A^3\Sigma_u^+(v'') \rightarrow B^2\Sigma_u^+(v')$.

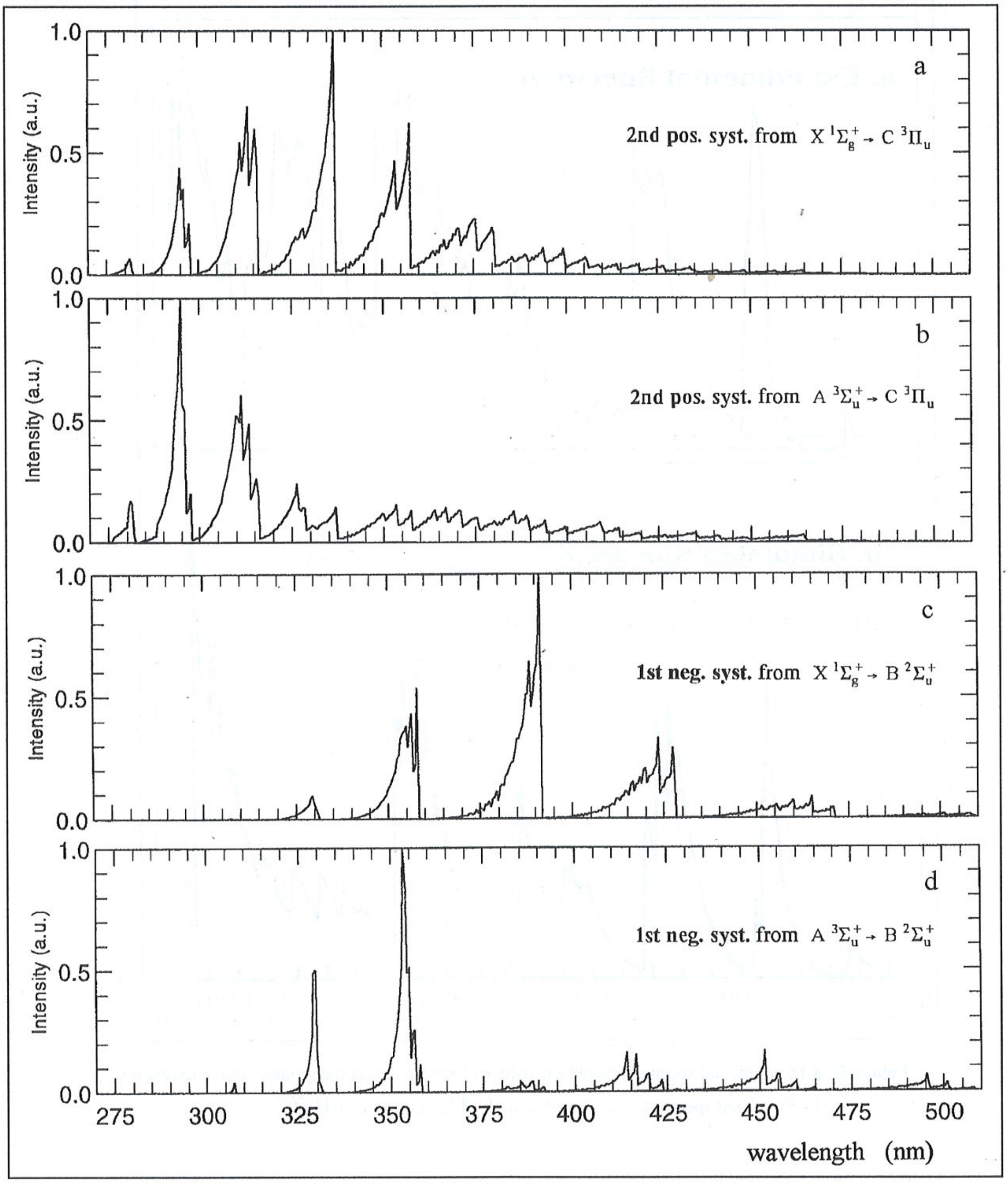

Figure 4: Simulated spectra, assuming a 100% production :

-a- of (2s+) of N_2 from ground state $X^1\Sigma_g^+$

- **b-** of (2s+) of N_2 from metastable state $A^3\Sigma_u^+$

- **c-** of (1s-) of N_2 from ground state $X^1\Sigma_g^+$.

- **d-** of (1s-) of N_2 from metastable state $A^3\Sigma_u^+$.

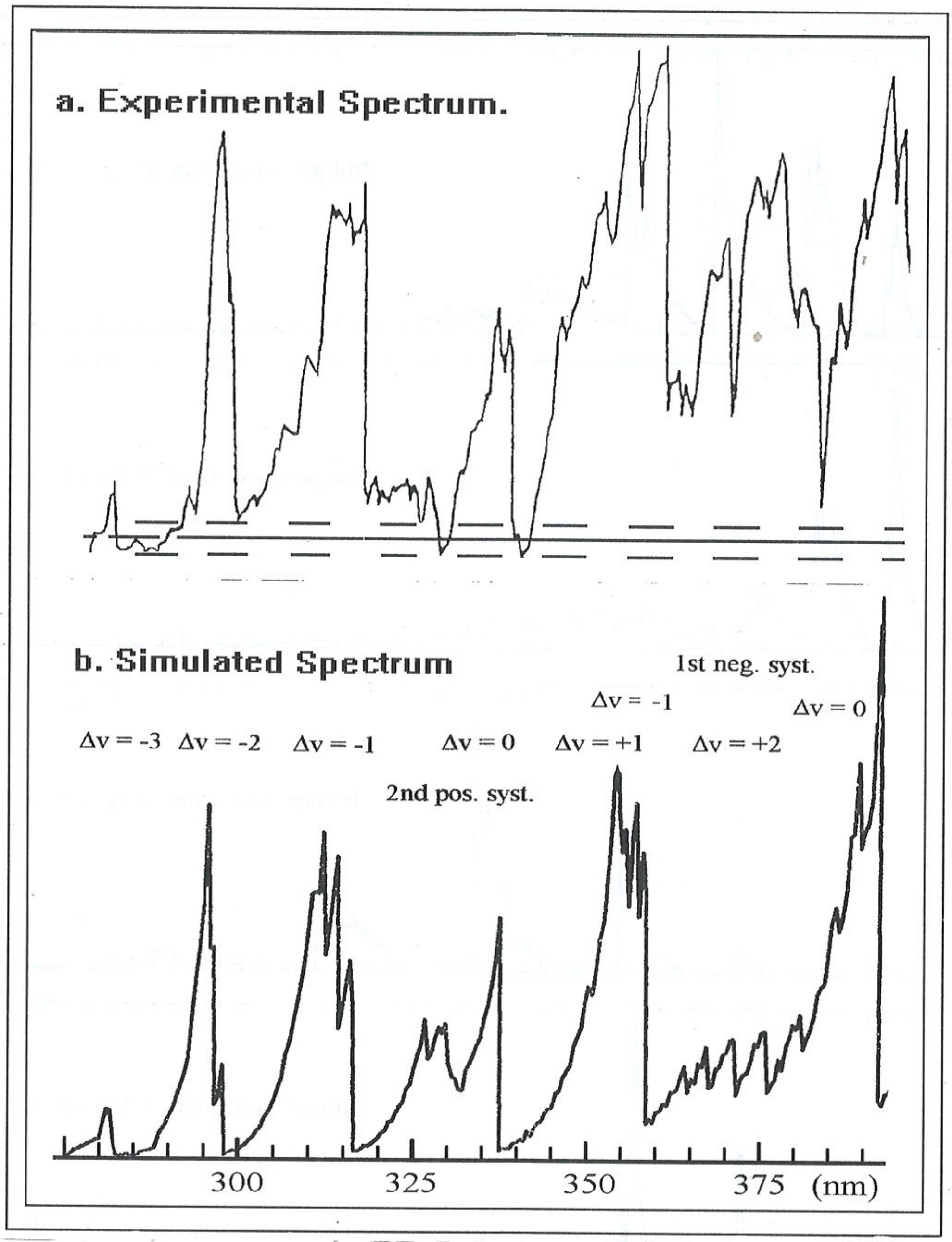

Figure 5: **a**-Experimental spectra showing intensity of band's heads at the moment of arc extinction.
b- Simulated spectra formed by 60% of $C^3\Pi_u$ and 40% of $B^2\Sigma_u^+$.

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