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N(²D) and N(²P) metastable production by electron collisions in a D.C. glow discharge

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Résumé. — Les densités des atomes métastables d'azote atomique N(²D) et N(²P) ont été mesurées par absorption optique dans une décharge lumineuse continue. La densité électronique a été mesurée à l'aide d'une cavité hyperfréquence. L'évolution des densités des deux états N(²D) et N(²P) en fonction de la densité électronique permet d'estimer le coefficient de création global C_e^M des niveaux métastables par collisions électroniques : $e + N_2 \xrightarrow{C_e^M} e + N(^2D, ^2P) + N$. Ce coefficient est du même ordre de grandeur pour N(²D) et N(²P). Il est compris entre $1,5 \times 10^{-10}$ et $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ pour des pressions variant de 0,5 à 1,5 torr (rayon du tube $R = 1 \text{ cm}$). Pour des courants supérieurs à 20 mA, la densité du niveau N(²P) est plus élevée que celle du niveau N(²D) (environ le double à 50 mA).

Abstract. — The atomic nitrogen metastable densities of N(²D) and N(²P) have been measured by optical absorption in a continuous glow discharge. Electronic densities have been measured with a microwave resonant cavity. The evolution of N(²D) and N(²P) densities as a function of electronic density allows the estimation of the overall creation coefficient by electronic collisions C_e^M : $e + N_2 \xrightarrow{C_e^M} e + N(^2D, ^2P) + N$. This coefficient is of the same order of magnitude for N(²D) and N(²P) and lies between 1.5×10^{-10} and $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for a pressure range between 0.5 and 1.5 torr (tube radius $R = 1 \text{ cm}$). For currents higher than 20 mA the density of N(²P) is larger than the N(²D) density (approximately a factor of two at 50 mA).

1. **Introduction.** — Metastable atoms N(²D, ²P) play an important role in the chemistry of upper atmosphere and laboratory plasmas. These states are located 19,233 and 28,839 cm^{-1} (2.38 and 2.58 eV) over the fundamental level N(⁴S) as shown in figure 1.

In the high atmosphere, these levels produce nitrogen oxides according to the reaction :

with $K_1(N ^2D) = 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [1]

$K_1(N ^2P) < 2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [2].

The reaction (1.1) is strongly exothermic and produce nitrogen oxides in excited vibrational states [3].

In plasma chemistry, the reaction (1.1) contributes to the synthesis of nitrogen oxides produced by electrical in nitrogen-oxygen mixtures.

The following reactions occur in nitrogen-hydrogen mixtures :

with $K_2(N ^2D) = 1.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [4]

$K_2(N ^2P) < 8 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ [2].

N(²D) states are generally more reactive than N(²P) states [4a] as it has been explained by Donovan and Husain [4b]. As a matter of fact, there is no exothermic adiabatic way for the reaction N(²P) + H₂ but there is one for the reaction N(²D) + H₂ producing NH* + H.

Concentrations of metastable atoms have been previously measured by optical absorption in a low power ($\approx 20 \text{ W}$) H.F. flowing afterglow in He-Ar mixtures containing from 0.5 to 4.3 % of N₂ with a total pressure ranging from 7 to 15 torr [1]. In this

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Fig. 1. — The first energy levels of nitrogen.

experiment, Lin and Kaufmann [1] have obtained the following concentrations :

— fundamental nitrogen atoms

$$N(^4S) \simeq 1 \text{ to } 2 \times 10^{14} \text{ cm}^{-3}$$

— metastable atomic nitrogen

$$N(^2D) \simeq 2.4 \times 10^{12} \text{ cm}^{-3}$$

$$N(^2P) < 4 \times 10^{11} \text{ cm}^{-3}.$$

In the same type of electrical discharge Foner and Hudson [5] have measured using a mass spectro-metric method, the relative concentration of metastable and fundamental atoms. They have obtained strong excited nitrogen atom concentrations in a mixture of He with 1 % N_2 at 2 torr :

$$N(^2D)/N(^4S) = 0.17 \text{ and } N(^2P)/N(^4S) = 0.06.$$

For the same pressure concentrations are weaker in pure nitrogen :

$$N(^2D)/N(^4S) = 6.8 \times 10^{-3}$$

and

$$N(^2P)/N(^4S) = 2.5 \times 10^{-3}.$$

Although several reactive transfers from $N(^2D-2P)$ have been studied nothing is known about the effective cross-sections production of these states by electronic collisions. Only effective cross-sections for excitation of radiative levels of atomic nitrogen are known [6, 7, 8].

The objective of this study is to determine the electronic excitation coefficients of the $N(^2D)$ and $N(^2P)$ states. Metastable atom densities have been measured by optical absorption, in the positive column of a continuous electrical discharge in pure nitrogen. Density evolutions of both states $N(^2D)$ and $N(^2P)$ have been studied as functions of the electron density.

2. Experimental. — Figure 2 shows the whole experimental device. Nitrogen is excited by a continuous glow-discharge in a 2 cm internal diameter, 50 cm long pyrex glass tube closed at both ends with MgF_2 windows. The tube is connected to a vacuum tank which permits a stable working pressure. This pressure is measured on the vacuum tank using a Pirani gauge calibrated for pure nitrogen. First the system is baked and pumped by a turbomolecular pump to an ultimate pressure of about 5×10^{-8} torr. The nitrogen gas utilized had an impurity level of 50 ppm. The dominant impurity was argon.

Fig. 2. — Experimental device.

At one of the tube's extremities is set the ultra-violet light source. It is a Penning discharge (Damany source from Jobin Yvon) which emits strong atomic nitrogen spectral lines.

The other side of the tube is in front of the entrance slit of a 50 cm focal length vacuum ultra-violet monochromator (ASM 50 Jobin Yvon) using a 1200 lines/mm holographic toroidal grating. The apparatus profile is asymmetrical with a width of $1.3 \text{ \AA}$ [9]. A sodium salicylate scintillator placed behind the exit slit convert the ultra-violet light to a continuous spectrum around $4000 \text{ \AA}$ [10], which is detected with a photomultiplier (RTC 56 UVP).

The electron density is measured by the frequency shift of a resonant cavity tuned to the TM_{020} mode [11]. The cavity is excited by a sweep oscillator (Hewlett Packard 692 A).

The gas temperatures in the light source and in the discharge have been calculated from the intensity

distribution of the rotational spectrum of molecular nitrogen [12]. This rotational structure is observed using a 150 cm focal length monochromator with a resolution of about 5×10^{-2} Å at 4 000 Å.

3. Measurement of N(²D) and N(²P) concentrations by optical absorption. — Metastable levels concentrations have been determined from light absorption by using the Mitchell and Zemansky [3] method.

Figure 1 shows N(²D) and N(²P) levels and radiative transitions which lead to these levels. Transitions coming from upper levels are doublet separated by about 2 Å and each of them (except 1 494.67 Å) exhibits a fine structure.

For an absorption length L , the absorption is

$$A_L = 1 - \frac{I_t}{I_0}, \quad (3.1)$$

where I_0 and I_t are the incident and transmitted intensities.

Taking into account the fine structure, the absorption is

$$A_L = 1 - \frac{\int_0^\infty \left[\sum_i I_{0i}(\lambda) \right] \exp\left(-L \sum_i k_i(\lambda)\right) d\lambda}{\int_0^\infty \sum_i I_{0i}(\lambda) d\lambda}. \quad (3.2)$$

The integration is performed over the whole line profile. The i subscript represents each component of the fine structure. $\sum_i L k_i(\lambda)$ is the optical depth,

I_{0i} the incident intensity and k_i the absorption coefficient given by [13] :

$$k_i(\lambda) = k_i(\lambda_{i0}) F_i(\lambda), \quad (3.3)$$

where λ_{0i} is the wavelength at the center of the line and $F_i(\lambda)$ represents the Voigt profile which is the convolution of a gaussian profile (Doppler effect) and of a Lorentzian profile (natural broadening).

For each component of the fine structure, the natural broadening is :

$$\Delta\lambda_N = \frac{\lambda^2}{2\pi c} \sum_{m < n} A_{nm} \quad (3.4)$$

and the relative Doppler broadening

$$\frac{\Delta\lambda_D}{\lambda_D} = 7.16 \times 10^{-7} \left(\frac{T}{M} \right)^{1/2}. \quad (3.5)$$

In these expressions the subscript m refers to the metastable level, and n to a radiative level, A_{nm} the transition probability from level n to m , c the speed of the light, T the atomic temperature and M the atomic mass.

The absorption coefficient $k_i(\lambda_{i0})$ at the center of the line i is given by [13] :

$$k_i(\lambda_{i0}) = \frac{e^2}{4\pi\epsilon_0 m_e c^2} 2\sqrt{\pi \ln 2} \frac{\lambda^2}{\Delta\lambda_D} n_i f_i. \quad (3.6)$$

In this expression e and m_e are the charge and the mass of the electron, ϵ_0 the permittivity of vacuum, f_i is the oscillator strength of the component i and n_i the absorbing level density which is equal to the total metastable level density (²D or ²P) balanced by the statistical weights of each component of the fine structure. In MKS units, eq. (3.6) gives :

$$k_i(\lambda_{i0}) = 8.31 \times 10^{-15} \frac{\lambda^2}{\Delta\lambda_D} n_i f_i. \quad (3.7)$$

The data used are listed in table I, where the transitions probabilities come from reference [14].

Table I. — Spectroscopic data for N(²D, ²P) absorption lines from [14].

λ_{nm} (Å)	A_{nm} (10^{-8} s^{-1})	$\sum_{m < n} A_{nm}$ (10^{-8} s^{-1})	g_m	f_{nm}
1 492.62	5.3	8.03	6	0.12
1 492.81	0.58	8.03	4	0.019
1 494.67	5.0	6.95	4	0.084
1 742.72	0.35	8.03	2	0.032
1 742.73	1.8	8.03	4	0.082
1 745.25	1.3	6.95	2	0.052
1 745.26	0.65	6.95	2	0.082

The apparatus profile of the V.U.V. monochromator is asymmetrical [9]. We have calculated the convolution product of this profile with the line profile. The whole calculation that relates A_L (eq. (3.2)) to the metastable density is performed numerically for a 50 cm absorption length and for several temperatures of the source and of the discharge.

Source and absorbing media temperatures have been determined from the rotational distribution of the second positive band,

$$[C^3\Pi_u(v=0) \rightarrow B^3\Pi_g(v=0)],$$

at 3 371 Å. Usually in glow discharges, the rotational temperature is equal to the discharge temperature. In some cases, collisions between excited nitrogen molecules can disturb the $C^3\Pi_u$ rotational band distribution. For instance Ockim *et al.* [15] have observed transfers from N₂(E²Σ_g⁺) metastable states. This effect is observable on the spectrum of the second positive band only if temperatures are below 300 K. We find $T_R \simeq 500$ K for the Damany source. For discharge pressures ranging between 0.5 and 1.5 torr, the rotational temperature changes from 400 K to 600 K when the discharge current varies from 0.5 to 50 mA.

We have found that, for the same metastable density and for a source temperature of 500 K the change of the calculated absorption A_L is less than 1 % when the discharge temperature varies from 400 to 600 K. As the accuracy of our absorption measurements is about $\pm 2\%$, we calculate the absorption for the same temperature of the source and the discharge. Figure 3 shows the variation of metastable densities *versus* absorption calculated for the strongest lines, for a discharge and source temperature of 500 K.

Fig. 3. — Metastables density *versus* absorption for discharge and source temperatures of 500 K.

4. Experimental results. — **4.1 ELECTRONIC DENSITY.** — Electronic density is measured from the frequency shift of a H.F. resonant cavity surrounding the discharge tube. The electrons of the discharge disturb the microwave field which induces a shift of the cavity resonance frequency [11]. The observed electron densities are relatively low ($\approx 10^9 \text{ cm}^{-3}$). A TM mode has been chosen because the electric field is maximum on the cavity axis. A numerical solution of the electromagnetic field equations gives the relation between the electronic density and the frequency shift. This equation takes into account the dimensions of the cavity and of the discharge tube, the glass thickness and the dielectric constant ($\epsilon = 4.45$ for Pyrex). In our case, for the TM₀₂₀ mode, the electronic density n_e is proportional to the frequency shift Δf if n_e does not exceed $4 \times 10^{10} \text{ cm}^{-3}$, so

$$n_e = 7 \times 10^8 \Delta f \quad (4.1)$$

where n_e is expressed in cm^{-3} and Δf in MHz.

The variations of n_e as function of current intensities are shown on figure 4 for several pressures. We notice that n_e is proportional to the discharge current up to 20 mA.

Fig. 4. — Electronic density *versus* discharge current intensity.

4.2 METASTABLE DENSITIES. — The optical absorption has been measured on the most intense lines corresponding to radiative transitions terminating on the metastable states concerned; the 1492.6 Å line for N(²D) and the 1742.7 Å line for N(²P). Metastable densities are deduced from the A_L absorption measurement using the graph of the figure 3.

Figures 5 and 6 present the N(²D) and N(²P) density variations *versus* discharge current for different pressures. For currents lower than 10 mA the metastable densities increase linearly with the current, and the slope increase with the pressure.

Fig. 5. — N(²D) density *versus* discharge current intensity.

Fig. 6. — N(²P) density versus discharge current intensity. Fig. 7. — N(²D) density versus electronic density n_e .

Since the discharge current is related to the electronic density, the metastable densities variations can be expressed as functions of n_e (Figs. 7 and 8). First, densities of both states increase linearly with n_e and then lead to a saturation for which the N(²P) level is more populated than the N(²D).

5. Discussion. — **5.1 BALANCE OF METASTABLE ATOMS.** — Metastable atoms are created by electronic collisions, radiative cascade from upper excited levels and electron-ion recombination and are destroyed by diffusion to the wall, collisions with the neutrals, electronic collisions and collisions between metastables.

The metastable creation rate by electronic collisions is

$$\left(\frac{dn_M}{dt}\right)_{e-0} = n_e n_0 C_e^M \quad (5.1)$$

where n_0 is the neutral gas density and C_e^M the overall creation coefficient by electrons. This coefficient includes the direct and stepwise processes which contribute to populate the nitrogen metastable atoms. C_e^M is *a priori* a function of the ratio n_e/n_0 and of the electron temperature T_e . By analogy with rare gases [20], C_e^M can be estimated to be of the order of 10^{-10} to 10^{-11} cm³ s⁻¹. As $n_0 \sim 10^{16}$ cm⁻³ (at 1 torr) and $n_e \sim 10^9$ cm⁻³ the term (5.1) is of the order of 10^{14} - 10^{15} cm⁻³ s⁻¹.

The electron-ion recombination creation rate is proportional to n_e^2 and to the recombination coefficient α :

$$\left(\frac{dn_M}{dt}\right)_{\text{rec.}} = \alpha n_e^2. \quad (5.2)$$

Fig. 8. — N(²P) density versus electronic density n_e .

Biondi [19] has shown that the α coefficient decreases strongly when the electronic temperature T_e increases : $\alpha = 2.5 \times 10^{-7}$ cm³ s⁻¹ at $T_e = 300$ K and $\alpha \sim 2 \times 10^{-8}$ cm³ s⁻¹ at $T_e = 10^4$ K. In a positive column, T_e is always greater than 10^4 K. If we suppose that all the electron - N₂⁺ ion recombinations lead to atomic nitrogen metastable levels, the term (5.2) is of the order of 2×10^{10} cm⁻³ s⁻¹ since $n_e \sim 10^9$ cm⁻³. Consequently the metastable creation due to recombination remains negligible compared with the electronic excitation.

The radiative cascade coming from upper excited levels is taken into account in the electronic creation coefficient C_e^M .

In a positive column the radial distribution of metastables is generally a Bessel function. Since the metastables are destroyed on the tube wall, then the diffusion loss term is :

$$\left(\frac{dn_M}{dt}\right)_{\text{diff.}} = n_M \frac{D_M}{\Lambda^2} \quad (5.3)$$

where D_M is the metastable diffusion coefficient, $\Lambda = (R/2.4)$ is the diffusion length and R the tube radius.

Destruction rates by neutral and electronic collisions are respectively given by

$$\left(\frac{dn_M}{dt}\right)_{M-0} = n_M n_0 C_M^0 \quad (5.4)$$

$$\left(\frac{dn_M}{dt}\right)_{M-e} = n_M n_e C_M^e \quad (5.5)$$

where C_M^0 and C_M^e are respectively destruction coefficients by neutral and electronic collisions.

The metastable-metastable collisions can only give recombination on an excited state of the N_2 molecule, because ionization of nitrogen atom is not energetically possible. This effect has to be considered only at high metastable densities ($n_M > 10^{11} \text{ cm}^{-3}$).

Under steady-state conditions (for $n_M < 10^{11} \text{ cm}^{-3}$) where the metastable creation rate is equal to the destruction-rate, then the metastable density is given by :

$$n_M = \frac{n_e n_0 C_e^M}{\frac{D_M}{\Lambda^2} + n_0 C_M^0 + n_e C_M^e} \quad (5.6)$$

5.2 ELECTRONIC CREATION COEFFICIENT. — Experimental curves in figures 7 and 8 indicate that the $N(^2D)$ and $N(^2P)$ densities increase linearly with n_e at low electronic densities. Since n_e is low, the electronic destruction term can be neglected in eq. (5.6). This equation can be written :

$$\frac{n_M}{n_e} = \frac{n_0 C_e^M}{\frac{D_M}{\Lambda^2} + n_0 C_M^0} = a_M \quad (5.7)$$

where a_M is a constant given by the slope at the origin of the experimental curve n_M versus n_e . From this experimental result we deduce, first that, the electronic coefficient C_e^M is independent of n_e ; i.e. that the dissociative excitation of the nitrogen metastable appears to be a direct process or a two steps process with an intermediate state independent of n_e . Second that C_e^M can be determined from the experimental a_M values if the destruction frequencies D_M/Λ^2 and $n_0 C_M^0$ are evaluated.

The vacuum tank maintains the pressure P constant in the tube. So the nitrogen molecular density n_0 varies with gas temperature T following the perfect gas law : $n_0 = P/kT$.

The destruction rate C_M^0 have been measured by different authors for both levels $N(^2D)$ and $N(^2P)$. Those values are collected in table II. There is a good agreement for $N(^2D)$ but for $N(^2P)$, $C_M^0(^2P)$ is ranging from 10^{-16} to $6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. The most recent values have been selected :

$$C_M^0(^2D) = 1.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \quad [16]$$

$$C_M^0(^2P) = 1 \text{ to } 3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} \quad [17].$$

Table II. — Neutral quenching coefficients for $N(^2D-^2P)$.

$C_M^0(^2D)$ ($\text{cm}^3 \text{ s}^{-1}$)	$C_M^0(^2P)$ ($\text{cm}^3 \text{ s}^{-1}$)	Reference
$\leq 6 \times 10^{-15}$	$< 3 \times 10^{-19}$	[23]
$1.6-2 \times 10^{-14}$	6×10^{-14}	[1]
1.5×10^{-14}	10^{-16}	[24]
1.8×10^{-14}		[16]
	$1-3 \times 10^{-16}$	[17]

The diffusion coefficient of atomic nitrogen in molecular nitrogen $D(N, N_2)$ has been measured [18] : $D(N, N_2) P = 221 \text{ cm}^2 \text{ s}^{-1} \text{ torr}$ at 280 K where P is the gas pressure. Because diffusion coefficients $D_M(^2D, N_2)$ and $D_M(^2P, N_2)$ are not known, we have used the $D(N, N_2)$ value. The product DP (diffusion coefficient $\times$ pressure) is proportional to $T^{3/2}$ [18]. At $T = 500 \text{ K}$, the diffusion coefficients chosen are :

$$D_M(^2D, N_2) P = D_M(^2P, N_2) P = 527 \text{ cm}^2 \text{ s}^{-1} \text{ torr}.$$

In the table III are reported, for different pressures, the estimated value of D_M/Λ^2 , $n_0 C_{2D}^0$, the measured $a_M(^2D)$ and $a_M(^2P)$ slopes and the deduced C_e^{2D} and C_e^{2P} coefficients. The diffusion frequency D_M/Λ^2 and the quenching frequency of $N(^2D)$ are respectively of the order of $3 \times 10^3 \text{ s}^{-1}$ and $3 \times 10^2 \text{ s}^{-1}$.

The quenching rate of $N(^2P)$ is two order of magnitude smaller than the $N(^2D)$. The quenching of $N(^2P)$ by N_2 molecules is negligible with respect to the diffusion. We found that C_e^{2D} and C_e^{2P} are of the same order of magnitude and decrease from 1.5×10^{-10} to $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ when the pressure increases from 0.5 to 1.5 torr.

The experimental determinations of C_e^{2D} and C_e^{2P} are very sensitive to the neutral gas temperature, because they are calculated from eq. (5.7) where n_0 and D_M are functions of T . For instance, we have seen that

$$C_e^{2P} = a_M(^2P) \frac{D_M/\Lambda^2}{n_0}.$$

Table III. — *Estimated diffusion and quenching frequencies, measured slopes and electronic creation coefficients for N(²D) and N(²P) (Relative error $\Delta C/C \sim 50\%$).*

P (torr)	D/Λ^2 (s ⁻¹)	$n_0 C_{2D}^0$ (s ⁻¹)	$a_M(^2D)$	$a_M(^2P)$	C_e^{2D} (cm ³ s ⁻¹)	C_e^{2P} (cm ³ s ⁻¹)
0.5	6.08×10^3	1.74×10^2	1.85×10^2	2.46×10^2	1.2×10^{-10}	1.6×10^{-10}
0.6	5.06×10^3	2.09×10^2	1.63×10^2	2.22×10^2	7.4×10^{-11}	9.7×10^{-11}
0.7	4.34×10^3	2.43×10^2	2.5×10^2	2.57×10^2	8.5×10^{-11}	8.3×10^{-11}
0.8	3.80×10^3	2.77×10^2	2.07×10^2	2.93×10^2	5.5×10^{-11}	7.2×10^{-11}
0.9	3.38×10^3	3.13×10^2	3.45×10^2	3.45×10^2	7.3×10^{-11}	6.7×10^{-11}
1.0	3.04×10^3	3.47×10^2	3.0×10^2	4.0×10^2	5.3×10^{-11}	6.3×10^{-11}
1.2	2.53×10^3	4.18×10^2	4.52×10^2	6.13×10^2	5.8×10^{-11}	6.7×10^{-11}
1.4	2.17×10^3	4.86×10^2	3.75×10^2	4.06×10^2	3.7×10^{-11}	3.3×10^{-11}
1.5	2.03×10^3	5.22×10^2	5.62×10^2	6.25×10^2	5.0×10^{-11}	4.4×10^{-11}

For a fixed pressure we measure the slope $a_M(^2P)$, we see that the deduced coefficient is a function of $T^{5/2}$. The temperature T is measured with an accuracy of ± 50 K, that gives an error of about $\pm 30\%$ on $T^{5/2}$. The accuracy of the a_M measurement is about 20%. The determination of the coefficients C_e^{2D} and C_e^{2P} is made with an accuracy of about 50%.

The results can be compared to those found for argon [20] for $n_0 R \sim 10^{16}$ cm⁻²

$$C_e(^3P_2) = 2 (\pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

$$C_e(^3P_0) = 3 (\pm 1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}.$$

For $n_0 R \sim 10^{16}$ cm⁻², in the Maxwell distribution approximation for the electron energy, the electronic temperatures are of the order of 2 eV in argon and nitrogen. Argon and atomic nitrogen metastable levels are located about 12 eV above the ground level ($N_2(X^1\Sigma_g^+)$ for nitrogen).

Although excitation conditions are nearly the same in the two gases, we found that electronic-creation coefficient C_e^{2D} and C_e^{2P} in nitrogen are greater than those of metastable argon.

We can also notice that the exchange

by electron collisions can be neglected. With this exchange process, the $N(^2D)$ electron collisions creation term is :

$$\frac{dn(^2D)}{dt} = n_e(n_0 C_e^{2P} + n(^2P) C_e^{2D}). \quad (5.8)$$

By analogy with rare gas, for instance helium [21] for which the two metastable levels are separated by 0.8 eV, the exchange coefficient would be

$$C_{2P}^{2D} \sim 10^{-6} - 10^{-7} \text{ cm}^3 \text{ s}^{-1}.$$

The product $n(^2P) C_e^{2D}$ is of the order of 10^5 to

10^4 s⁻¹ and can be neglected when compared with $n_0 C_e^{2P} \sim 10^6$ s⁻¹.

Figures 7 and 8 show that for electron densities $n_e > 10^9$ cm⁻³ the metastable densities are nearly saturated. This effect could be described by the eq. (5.6) when the electronic collisions are the dominant loss term. Then the saturated metastable densities n_M^s could be written :

$$n_M^s = \frac{n_0 C_e^M}{C_M^e}. \quad (5.9)$$

The ratio C_e^M/C_M^e of the electronic coefficients could be deduced from the n_M^s and n_0 measurements. But, in this high electron density range the variation of each coefficient with n_e remains unknown. Metastable-metastable collisions may become efficient in this nearly saturated range where $n_M > 10^{11}$ cm⁻³, then eq. (5.9) would not be valid. Furthermore, the relative contribution of direct and stepwise process must be studied accurately in this high electron and metastable densities range before calculating the C_M^e coefficient.

6. Conclusion. — We have determined the $N(^2D, ^2P)$ metastable atomic concentration in a N_2 glow discharge ($R = 1$ cm) for current intensities $2 < I < 50$ mA and pressures $0.5 < p < 1.5$ torr. In the range $10 < I < 50$ mA, the atoms concentration $N(^2P)$ is higher than that of $N(^2D)$. Lin-Kaufman [1] and Foner-Hudson [5] have found opposite results in mixtures of rare gas-nitrogen at higher pressures. In the present pure N_2 discharges, the electrons collisions are efficient processes to excite and dissociate molecular nitrogen. Consequently, the following reaction has to be taken into account in the production of $N(^2P)$ states [2, 22] :

with

$$k_N = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ at } 300 \text{ K} \quad [22].$$

At low electronic densities ($n_e < 2 \times 10^8 \text{ cm}^{-3}$), the $N(^2D, ^2P)$ densities increase linearly with n_e . We deduce from this variation that the electronic creation coefficients of the atomic metastable states C_e^{2D} and

C_e^{2P} are independent of the electronic density. The values obtained for the two coefficients are on the same order of magnitude and decrease as the pressure increase.

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