Some Aspects in Recombining Transient Nitrogen Plasmas

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The temporal evolution of the population densities of a monatomic Nitrogen plasma has been studied in the electron temperature range $0.5\,\text{eV} \leqq kT_e \leqq 1\,\text{eV}$ and in the electron number density interval $10^{12}\,\text{cm}^{-3} \leqq n_e \leqq 10^{14}\,\text{cm}^{-3}$ by solving a coupled system of master equations. The results show that the times necessary to achieve quasi-stationary conditions for the population densities can be as long as 10^{-5} sec. in the optically thick plasma, and two order of magnitude shorter in the optically thin case. The possibility of population inversions during the recombination of a completely ionized Nitrogen plasma ($n_e \simeq 10^{15}\,\text{cm}^{-3}$, $kT_e = 0.5$ eV) is then shown.

1. Introduction

Population densities of electronic states of atoms in non thermal plasmas are commonly calculated by means of BKW (Bates, Kingston and McWirter) theory [1], which considers the populations of excited states in a quasi-stationary condition ($\partial n_i/\partial t = 0$, $i > 1$) with respect to the temporal evolution of the ground state and of the electrons ($\partial n_i/\partial t$, $\partial n_e/\partial t \neq 0$). This theory is usually applied to transient plasmas under the hypothesis of an almost instantaneous rearrangement of electronic states to the new quasi-stationary conditions. This assumption, however, can fail when the macroscopic times involved in the temporal variations of plasma parameters such as electron temperature and electron number density n_e are of the same order of magnitude as the relaxation times τ_i of the electronic states. This occurs for example in the expansion flow of ionized gases when the expansion times are of the order of $10^{-7} \ldots 10^{-6}$ sec.

Other possibilities of inapplicability of the BKW model arise when the plasma is subjected to laser pulses the duration of which are comparable with τ_i. In all these cases one must solve a coupled system of differential equations, describing the temporal evolution of excited states under the action of collisional and radiative processes. This technique has been applied to transient Helium [2], Hydrogen [3, 4] and Oxygen plasmas [5] by considering essentially the optically thin case. The results show that in the presence of metastable states (such as He(2s ^{3}S), O(3s ^{5}S)) the achievement of quasi-stationary condition occurs in times which can not be neglected as compared with other characteristic times.

In this work we consider the temporal evolution of electronic states of atomic Nitrogen plasmas in the electron temperature range $0.5\,\text{eV} \leqq kT_e \leqq 1\,\text{eV}$ and electron number densities ranging from 10^{12} to $10^{14}\,\text{cm}^{-3}$. Particular attention will be payed to optically thick plasmas, due to the fact that, when the reabsorption of a spectral line is complete, the electronic state of interest behaves as a metastable state. As a consequence the time necessary to achieve a quasi-stationary condition can be very long.

Finally the possibility of population inversions during the recombination of a completely ionized plasma will be presented and discussed.

2. Method of Calculation

The temporal evolution of the population density n_i of the i-th quantum state belonging to an atomic plasma can be written as:

$$\begin{aligned} \partial n_i/\partial t = {} & n_e \sum_{j \neq i} n_j K_{ji} + n_e^3 K_{ci} \\ & - n_i n_e \Big(K_{ic} + \sum_{j \neq i} K_{ij}\Big) \\ & + n_e^2 \beta_i + \sum_{j>i} n_j A_{ji} \\ & + n_i \sum_{j<i} (1-\lambda_{ij}) A_{ij} - n_i \sum_{j<i} A_{ij} \\ & - n_e^2 (1-\lambda_i) \beta_i - \sum_{j>i} n_j (1-\lambda_{ji}) A_{ji} . \end{aligned} \tag{1}$$

Equation (1) refers to a homogeneous transient plasma in which only radiative and electron collision processes are effective in populating and depopulating the levels. The rate coefficients appear-

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ing in Eq. (1) correspond to the following microscopic processes:

1) Collisional ionization and three body recombination:

$$e + N(i) \underset{K_{ci}}{\overset{K_{ic}}{\rightleftarrows}} e + N^+ + e\,.$$

2) Collisional excitation and deexcitation:

$$e + N(i) \underset{K_{ji}}{\overset{K_{ij}}{\rightleftarrows}} e + N(j)\,.$$

3) Spontaneous emission and reabsorption:

$$N(i) \underset{(1-\lambda_{ij})A_{ij}}{\overset{A_{ij}}{\rightleftarrows}} N(j) + h\nu\,.$$

4) Radiative recombination and photoionization:

$$N^+ + e \underset{(1-\lambda_i)\beta_i}{\overset{\beta_i}{\rightleftarrows}} N(i) + h\nu\,.$$

The λ_{ij} and λ_i parameters are related to the processes of photoabsorption and photoionization, respectively. They characterize the plasmas as optically thin for $\lambda_{ij} = \lambda_i = 1$ and optically thick for $0 \leqq \lambda_{ij}$, $\lambda_i < 1$ (see Ref. [6]). The system of differential equations typified by Eq. (1) can be solved by adding the auxiliary condition:

$$-\frac{\partial n_e}{\partial t} = \sum_i \frac{\partial n_i}{\partial t} = \gamma(t)\, n_e\, n^+\,, \tag{2}$$

and by considering the temperature as a parameter (see Ref. [2]).

It has been integrated by means of the algorithm of Ref. [7], which has been found much faster than the Runge-Kutta method utilized in our previous calculations.

The nitrogen energy diagram has been taken from Park [8]. It consists of 35 levels, some of which have been reported in Table 1 (the complete energy diagram can be found in Ref. [8]).

It can be noted that all levels but the first have been coalesced in different groups. The collisional rate coefficients (i.e. K_{ij} and K_{ic}) between all 35 levels, put into the analytical form by Park [8] and Catherinot and Sy [9]) have been used in the present paper. The rate coefficients for radiative processes (i.e. A_{ij} and β_i) have been taken from the same sources.

Table 1. Approximate energy diagram utilized in the present calculations.

Level number	
1	$2p^3\ ^4S^0$
2	$2p^3\ ^2D^0$
3	$2p^3\ ^2P^0$
4	$3s\ ^4P$
5	$3s\ ^2P$
6	$3p\ ^4S^0,\ ^4P^0,\ ^4D^0$
7	$3p\ ^2S^0,\ ^2P^0,\ ^2D^0$
8	$4s\ ^4P,\ ^2P$
9	$3d\ ^4P,\ ^4D,\ ^4F$
10	$3d\ ^2P,\ ^2D,\ ^2F$
11	$4p\ ^4S^0,\ ^4P^0,\ ^4D^0,\ ^2S^0,\ ^2P^0,\ ^2D^0$
12	$5s\ ^4P\ \ ^2P$
13	$4d\ ^4P,\ ^4D,\ ^4F,\ ^2P,\ ^2D,\ ^2F$
14	$4f\ ^4D^0,\ ^4F^0,\ ^4G^0,\ ^2D^0,\ ^2F^0,\ ^2G^0$
15	$5p\ ^4S^0,\ ^4P^0,\ ^4D^0,\ ^2S^0,\ ^2P^0,\ ^2D^0$
16	$6s\ ^4P,\ ^2P$

The energies, the statistical weight factors of the different levels as well as the completion of the energy diagram can be obtained in Reference [8].

3. Results

a) Population Densities

Case 1. ($n_e = 10^{12}$ cm^{-3}, $n_1 \simeq 10^{15}$ cm^{-3}, $b_i(t=0) = n_i/n_{i\,(\mathrm{Saha})} = 1$, $kT_e = 0.5$ eV).

Figure 1 shows the temporal derivatives of selected levels for the optically thin case. The plasma is in a typical recombination condition ($\partial n_e/\partial t < 0$) due to the radiative and three body collisional recombination. These reactions populate the first three levels, which present positive derivatives, while the other excited states ($i > 3$) have negative derivatives due to the spontaneous radiative transitions. As a consequence these last levels ($i > 3$) are underpopulated, as can be appreciated by Fig. 1 b, where the Saha deviations ($b_i = n_i/n_{i\,(\mathrm{Saha})}$) have been reported as a function of time. It should be noted that the first three levels do not change their initial population due to the fact that

$$\sum_{i=1}^{3} \Delta n_i \simeq \int_0^{10^{-4}} \frac{\partial n_e}{\partial t}\, dt \tag{3}$$

is small as compared with their initial populations.

An other interesting point is that the Saha deviations $b_i(t)$ reach their quasi-stationary values in a time of the order of $5 \cdot 10^{-7}$ sec (see Figure 1 b).

Figure 2 a, b reports similar results for an optically thick plasma (see Table 2). The behaviour

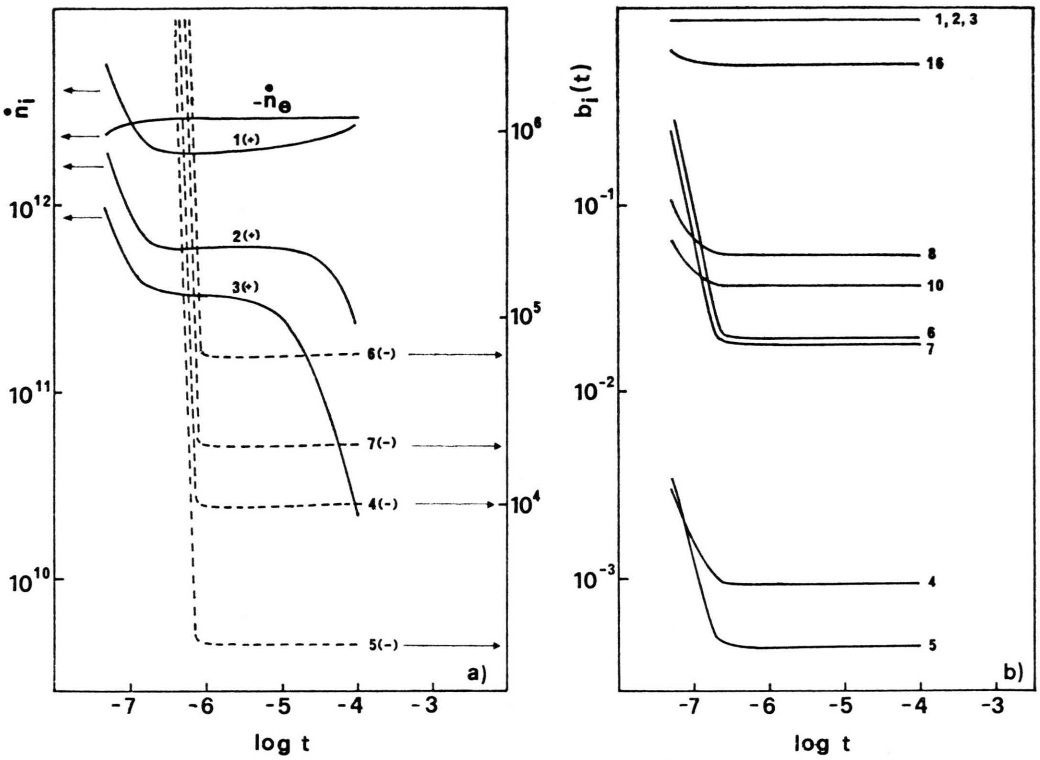

Fig. 1. a) Values of $\partial n_i/\partial t$ (cm^{-3} sec^{-1}) as a function of time for the optically thin plasma ($+ = \partial n_i/\partial t > 0$). b) Saha decrements $b_i(t) = n_i(t)/n_{i(\mathrm{Saha})}$ as a function of time for the optically thin plasmas ($n_e = 10^{12}$ cm^{-3}, $b_i(t=0) = 1$, $kT_e = 0.5$ eV, t in units see here and in the other figures; the numbers refer to the states of Table 1).

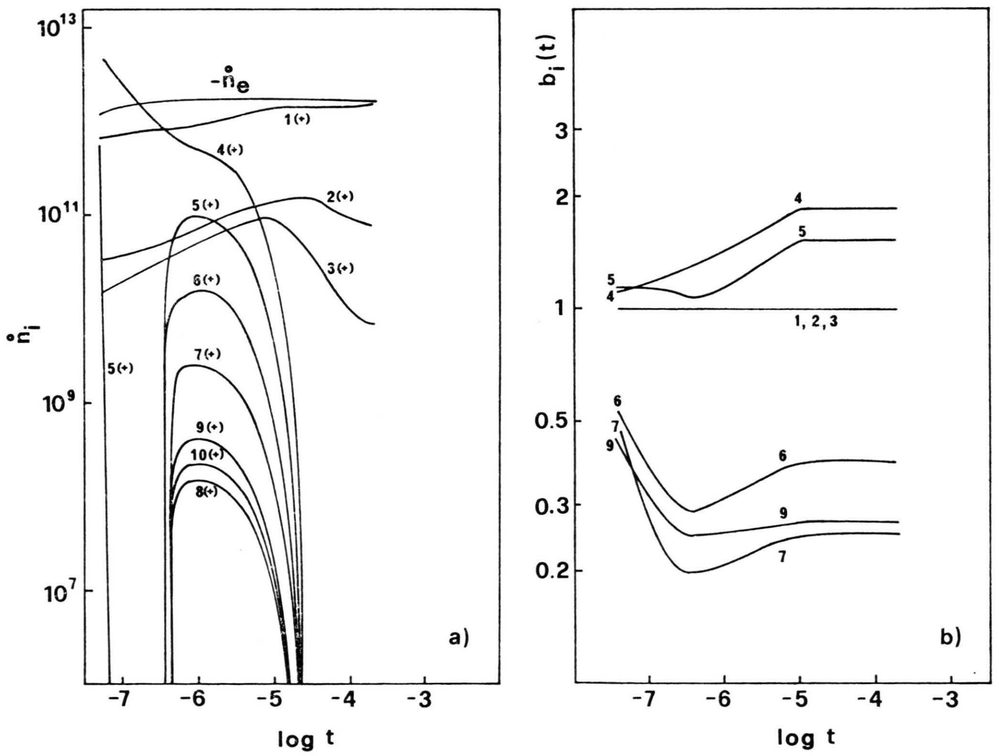

Fig. 2. a) Values of $\partial n_i/\partial t$ (cm^{-3} sec^{-1}) as a function of time for the optically thick plasma (see Table 2). b) Saha decrements $b_i(t) = n_i(t)/n_{i(\mathrm{Saha})}$ as a function of time for the optically thick plasma ($n_e = 10^{12}$ cm^{-3}, $b_i(t=0) = 1$, $kT_e = 0.5$ eV).

Table 2. Values of λ_i and λ_{ij} for the optically thick plasma.

$\lambda_i, \lambda_{ij} = 0$	for $i = 4, 5, 8, 9, 10, 12, 13, 16$ and $j = 1, 2, 3$

in this case is completely different from the previous case. It can be noted infact that after $t \simeq 5 \cdot 10^{-7}$ sec all levels present positive temporal derivatives. Typical is the behaviour of level 4 ($3s\,^4P$), the population of which strongly increases with time since it is now not radiatively connected with the ground state. The achievement of the quasi-stationary condition for this level will be reached when the collisional pumping rates from the ground state and the corresponding radiative pumping rates from the upper levels will be compensated by the collisional depopulating rates towards the neighbouring levels. These last processes are responsible of the increase of the population density of some levels after $t = 6 \cdot 10^{-7}$ sec. The situation described for the level $3s\,^4P$ in an optically thick plasma is very similar to behaviour of the metastable $3s\,^5S$ oxygen state in an optically thin plasma (see Ref. [5]). The time necessary to achieve the quasi-stationary conditions is of the order of 10^{-5} sec, which is two orders of magnitude longer than the corresponding one for the optically thin plasma.

The difference in the times necessary to achieve the quasi-stationary conditions in optically thin and thick plasmas can be understood by calculating the so called collisional-radiative relaxation time τ_{cr} of level 4 (i.e. level $3s\,^4P$). According to Ref. [10], one can estimate τ_{cr} in closed form by means of the equations

$$(\tau_{cr})_i{}^{-1} = (\tau_{ic})^{-1} + (\tau_{ir})^{-1}\,, \tag{4a}$$

where τ_{ic} represents the collisional relaxation time:

$$\tau_{ic} = \frac{1}{n_e\left(\sum\limits_{j<i} K_{ji} + \sum\limits_{j>i} K_{ji} + K_{ic}\right)} \tag{4b}$$

and τ_{ir} is the corresponding radiative one:

$$\tau_{ir} = 1/\sum_{j<i} \lambda_{ij}\, A_{ij}\,. \tag{4c}$$

For the level 4 in an optically thick plasma it can be shown that $\tau_{cr} \simeq \tau_{ic}$.

Applications of these formulas to the present case yield a ratio

$$(\tau_{cr})_{thick}/(\tau_{cr})_{thin} \simeq 10^2 \tag{5}$$

for level 4. This approximately reproduces the numerical calculation, even though the absolute values of relaxation times calculated by Eqs. (4a–c) are up to an order of magnitude smaller than those obtained by the solution of the system of master equations. These differences have been recently explained in Ref. [10].

Case 2 ($n_e = 10^{12}$ cm^{-3}, $n_1 \simeq 10^8$ cm^{-3}, $b_i(t=0) = 1$, $kT_e = 1$ eV).

This condition is very similar to that previously reported for $kT_e = 0.5$ eV for both optically thin and thick plasmas as can be appreciated by Figs. 3–4(a, b) and 5. In particular the quasi-stationary conditions are reached in times of the order of 10^{-7} and 10^{-5} sec for optically thin and thick plasmas respectively.

An interesting aspect of this condition can be observed for times of the order of 10^{-4} sec. At that time the Saha deviations of the first three quantum states strongly exceed the initial value $b_i(t=0) = 1$ ($i < 3$). This point can be understood by noting that now $\sum \Delta n_i$ ($i = 1 \ldots 3$) as calculated by Eq. (3) can not be neglected as compared with the initial values n_1, n_2, n_3. The fact that the population density of the ground state starts to deviate from its initial value for both optically thin and thick plasmas at the same time ($t \simeq 10^{-4}$ sec) can be justified by calculating the relaxation time of the ground state by means of the approximate formula (see Ref. [10])

$$\tau_1 \simeq \tau_e \simeq 1/n_e\, \gamma^{QSS}\,. \tag{6}$$

One obtains

$$(\tau_1)_{thick}/(\tau_1)_{thin} \simeq 1$$

in agreement with the numerical calculations.

Once more one should note that the absolute values of τ_1 as calculated from Eq. (6) and as given by the numerical solution are completely different. The strong increase of the b_i values ($i < 3$) for $t > 10^{-5}$ sec is reflected also on the other levels.

In particular levels 4 and 5, which lie near to the ground state, will benefit of the collisional pumping by increasing their number densities. This, in turn, is reflected also on the other levels (see Figure 5). Figure 6 shows the temporal evolutions of Saha deviations for selected levels starting from a different initial condition ($b_1(t=0) = b_2 = b_3 = 1$, $b_i(t=0) = 0$ for $i > 3$). It should be noted that the evolution goes toward the same quasi-stationary values $b_i{}^{QSS}$, since the $b_i{}^{QSS}$ depend only on n_e and

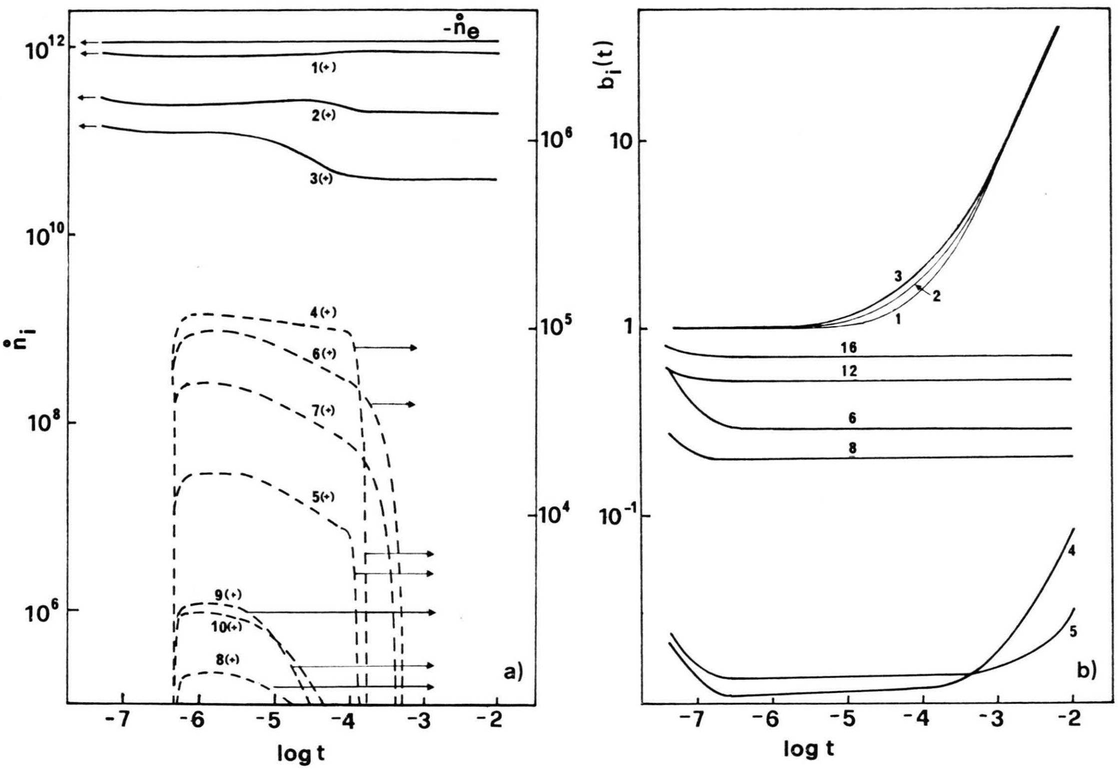

Fig. 3. a) Values of $\partial n_i/\partial t$ ($cm^{-3}\,sec^{-1}$) as a function of time for the optically thin plasma. b) Saha decrements $b_i(t) = n_i(t)/n_{i(\text{Saha})}$ as a function of time for the optically thin plasma ($n_e = 10^{12}\ cm^{-3}$, $b_i(t=0) = 1$, $kT_e = 1$ eV).

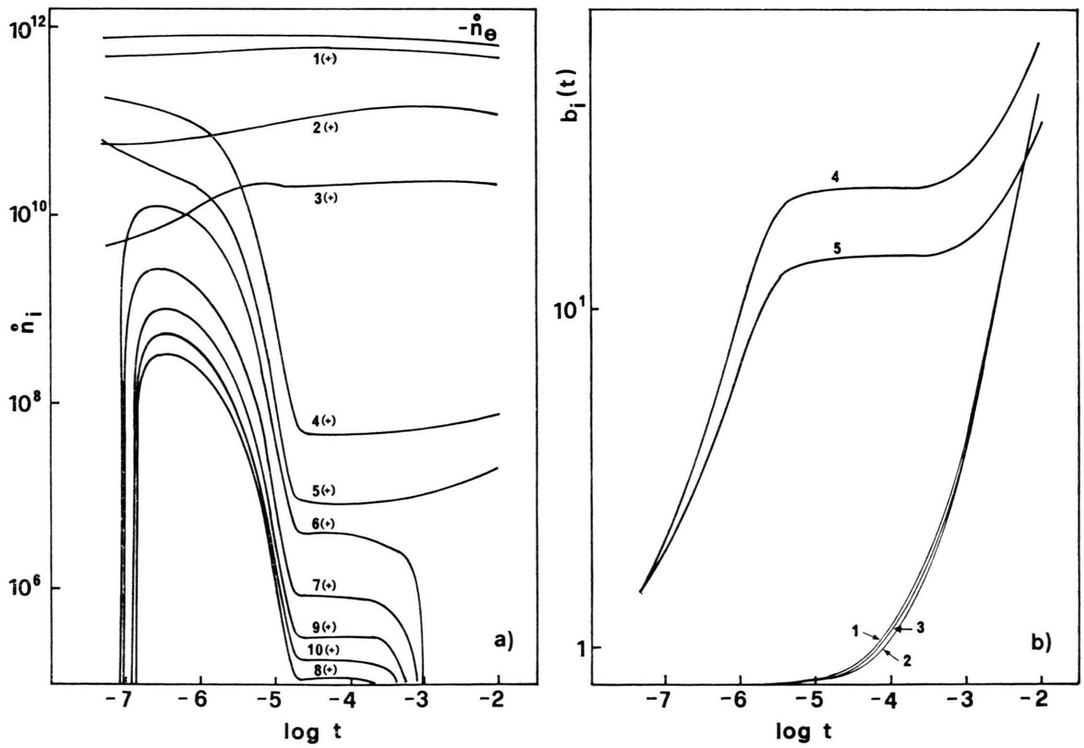

Fig. 4. a) Values of $\partial n_i/\partial t$ ($cm^{-3}\,sec^{-1}$) as a function of time for the optically thick plasma. b) Saha decrements $b_i(t) = n_i(t)/n_{i(\text{Saha})}$ as a function of time for the optically thick plasma ($n_e = 10^{12}\ cm^{-3}$, $b_i(t=0) = 1$, $kT_e = 1$ eV).

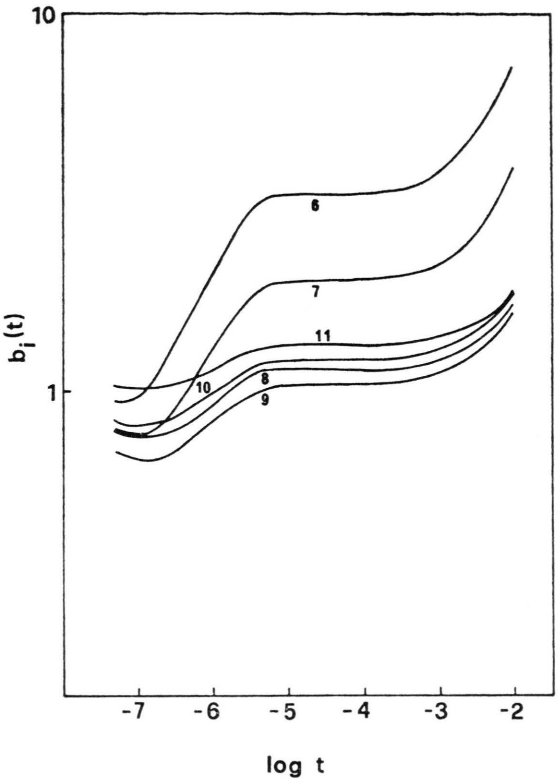

Fig. 5. Saha decrements $b_i(t) = n_i(t)/n_{i(\mathrm{Saha})}$ as a function of time for the optically thick plasma ($n_e = 10^{12}$ cm^{-3}, $b_i(t=0) = 1$, $kT_e = 1$ eV).

T_e and are independent of the choice of initial conditions. A comparison with the previous case shows strong differences in the early part of the evolution, as can be easily understood.

It is worth noting that the choice of the initial conditions for both cases 1—2 (i.e. a Saha equilibrium at the relevant T_e and n_e) has not a particular physical significance. However a different choice of initial conditions changes the absolute time scale and the absolute values of b_i but not the general behaviour previously reported.

b) $\gamma(t)$ Coefficients

Values of $\gamma(t)$ calculated by means of Eq. (2) with the aid of the numerical results have been drawn as a function of time for different conditions (Figure 7). It should be noted that the times necessary to achieve the quasi-stationary values γ^{QSS} are in general shorter than the corresponding times necessary to establish the quasi-stationary populations of excited states. This point is in agreement with the corresponding observations of Linbaugh and Mason [2] for Helium plasmas. It is interesting to compare the present γ^{QSS} values with the corresponding ones recently calculated for Oxygen plasmas [5]. It can be noted (see Table 3) that these coefficients do not differ too much despite the different energy diagrams and rate coefficients used in the two cases.

Table 3. A comparison of γ^{QSS} for optically thin and thick Nitrogen and Oxygen plasma ($kT_e = 1$ eV).

	$n_e = 10^{12}$ cm^{-3}	
	(a)	(b)
thin	$+ 0.117 \cdot 10^{-11}$	$+ 0.3 \cdot 10^{-12}$
thick	$+ 0.706 \cdot 10^{-12}$	$+ 0.2 \cdot 10^{-12}$
	$n_e = 10^{14}$ cm^{-3}	
	(a)	(b)
thin	$+ 0.351 \cdot 10^{-11}$	$+ 1.0 \cdot 10^{-12}$
thick	$+ 0.617 \cdot 10^{-12}$	$+ 0.8 \cdot 10^{-12}$

(a) Nitrogen plasma. (b) Oxygen plasma (Ref. [5]).

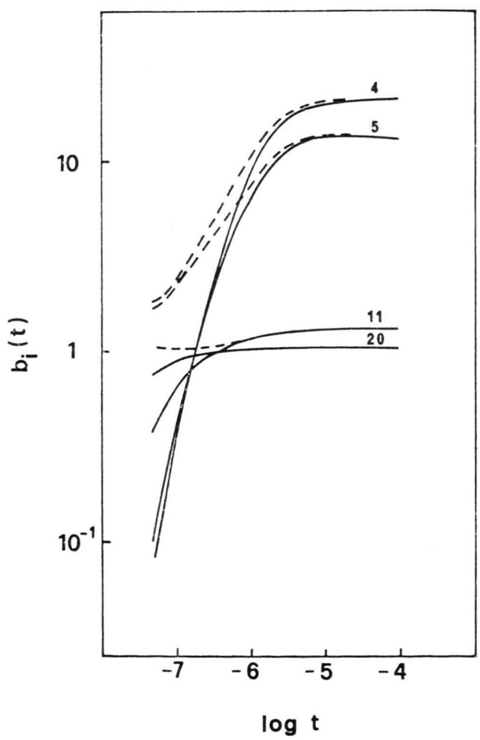

Fig. 6. Saha decrements $b_i(t) = n_i(t)/n_{i(\mathrm{Saha})}$ as a function of time for the optically thick plasma ($n_e = 10^{12}$ cm^{-3}, $kT_e = 1$ eV, full lines: $b_i(t=0) = 0$ for $i > 3$ and $b_i(t=0) = 1$ for $i = 1, 2, 3$; dashed lines: $b_i(t=0) = 1$ for all i.

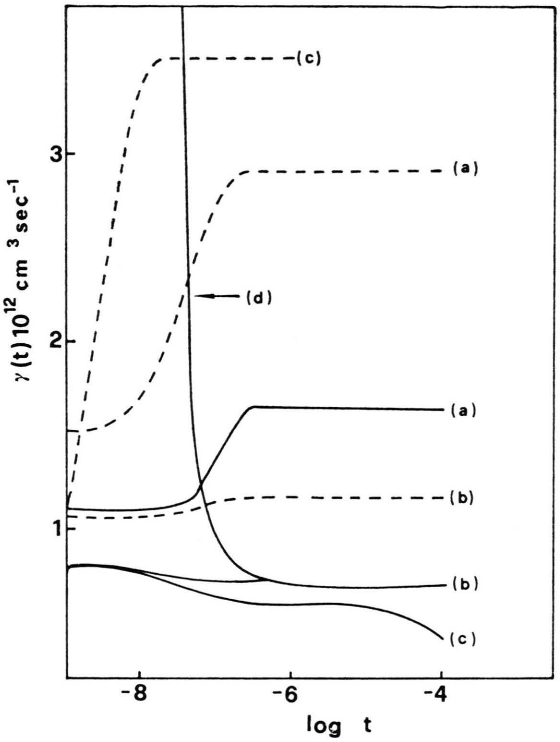

Fig. 7. Values of $\gamma(t)$ as a function of time for optically thin (dashed lines) and thick (full lines) Nitrogen plasmas. a) $n_e = 10^{12}$ cm^{-3}, $b_i(t=0) = 1$, $kT_e = 0.5$ eV; b) $n_e = 10^{12}$ cm^{-3}, $b_i(t=0) = 1$, $kT_e = 1$ eV; c) $n_e = 10^{14}$ cm^{-3}, $b_i(t=0) = 1$, $kT_e = 1$ eV; d) $n_e = 10^{12}$ cm^{-3}, $kT_e = 1$ eV, $b_i(t=0) = 0$ for $i > 3$ and $b_i(t=0) = 1$ for $i = 1, 2, 3$.

4. Population Inversions

An application of the present calculations is the prevision of population inversions during the recombination process. The results reported in the previous pages show no population inversions for the assumed initial conditions. However, let us consider a completely ionized Nitrogen plasma with $n_e = 10^{15}$ cm^{-3}, the temperature of which is suddenly decreased at $kT_e = 0.5$ eV. By following the temporal evolution of this plasma (see Fig. 8a and b) we can note population inversions of several excited states with respect to the ground state in a short transient phase ($10^{-11} \leqq t \leqq 10^{-9}$ for the optically thin plasma). This is due to the fact that the recombination processes first populate the higher electronic levels. The excitation, therefore, propagates along the excited states down to the ground one. During this transient phase, which must be short as compared with the relaxation times, population inversions can occur. It should be noted that the times at which the inversion of the different levels end, roughly follow the order of the relaxation times defined by Equations (4a–c).

Similar results have been obtained for the optically thick plasma (Figure 8b). In this case the magnitude of the inversion of the different levels as well as the times at which the inversions end are larger than the corresponding quantities for the optically thin plasma. The first point (i.e. $(n_i/g_i)_{\text{thick}} > (n_i/g_i)_{\text{thin}}$) can be understood by the fact that some radiative depopulating transitions are cancelled in the optically thick plasma, while the differences in the time scale can be understood on the basis of the differences in the relaxation times. As an example for level 4 we have for Eqs. (4a–c) $(\tau_{\text{cr}})_{\text{thick}}/(\tau_{\text{cr}})_{\text{thin}} \simeq 6$, which explains the fact that at $t = 10^{-9}$ sec the population of level 4 still overcomes the ground state only for the optically thick plasma.

The behaviour reported above is in line with the work of Ali and Jones [11] for hydrogenic plamas and with the work of Tallents [12] for C^{+5} plasmas (see also Ref. [13]). It should be noted that apparently Ali and Jones choosed as initial conditions ($t = 0$) completely ionized plasmas, while Tallents choosed quasistationary conditions at $t = 0$.

Studies performed in our laboratory show that the choice of initial conditions only affects the early part of the evolution, without affecting the bulk of results. A more serious problem in this kind of inversions lies, however, in the experimental way of suddenly decreasing the electron temperature.

5. Concluding Remarks

The temporal study of Nitrogen population densities as well as of the collisional-radiative recombination coefficients reported in the previous pages shows that the times necessary for the population densities to achieve the quasi-stationary conditions can be very long in optically thick plasmas (up to 10^{-5} sec) while they are two orders of magnitude smaller in optically thin plasmas. These times must be taken into account when one uses the quasi-stationary approximation for calculating the Saha deviations. On the contrary the times necessary to obtain quasi-stationary values for $\gamma(t)$ are very short in both optically thin and thick Nitrogen plasmas. As an application of the present calculations, we have shown the possibility

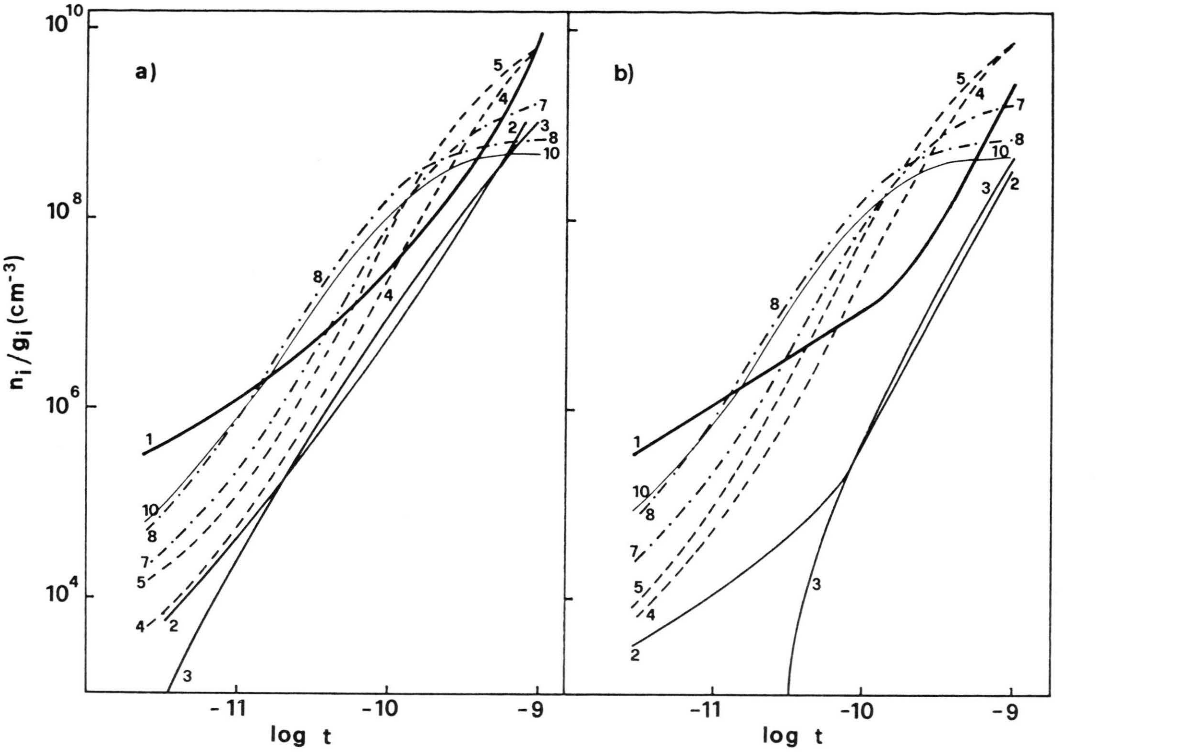

Fig. 8. Population densities (cm^{-3}) of selected levels for optically thin (a) and thick (b) Nitrogen plasma during the recombination of a completely ionized plasma ($n_e(t=0) \cong 10^{15}$ cm^{-3}, $n_i(t=0) = 0$ for all i, $kT_e = 0.5$ eV) (g_i: statistical weight factor).

of population inversions during the recombination of highly ionized plasmas.

The duration of these inversions is short as compared with the relaxation times of the excited states.

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