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Relaxation of the vibrational distribution function in N₂ time varying discharges

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Résumé. — La relaxation des fonctions de distribution des électrons et des molécules d'azote vibrationnellement excitées a été calculée en fonction du temps de résidence des espèces dans la décharge et dans la post-décharge. Dans la décharge, la température vibrationnelle croît avec le temps de résidence pour $t < 10^{-2}$ s. Dans la post-décharge, la fonction de distribution vibrationnelle de l'azote évolue pour présenter une surpopulation des niveaux élevés qui compense une dépopulation des bas niveaux.

Abstract. — Relaxation of the electron and vibrational distribution functions have been calculated in function of residence time in nitrogen electrical discharges and post-discharges.

In the discharge the vibrational temperature get bigger with the residence time for $t < 10^{-2}$ s. In the post-discharge the vibrational distribution is evolving in such a manner that the high levels are overpopulated as the low vibrational level population is dropping.

1. Introduction. — Many experimental works have appeared in these last years on the determination of the vibrational distribution of the electronic fundamental state $N_2(X^1\Sigma_g^+, V)$ in time varying [1] or flowing [2, 3] post-discharges by using lasers [1], electron beams [2] or metastable atoms [3] excited fluorescence as diagnostic techniques. The measured vibrational distributions are then thought representative of the vibrational distributions in the discharge. This point needs a theoretical justification since after the end of the discharge the vibrational distribution $N_2(X, V)$ undergoes a temporal relaxation, which in general yields highly non equilibrium vibrational distribution.

For this purpose we have calculated the vibrational distributions $N_2(X, V)$ in the discharge as a function of time as well as the relaxation of $N_2(X, V)$ in the post-discharge. Such a calculation allows us to compare the vibrational distributions in the discharge and post-discharge regimes and to assess the validity of the above mentioned assumption.

2. Vibrational distributions in electrical discharges. — The vibrational distribution $N_2(X, V)$ in the discharge can be calculated by solving a system of

vibrational master equations coupled to the Boltzmann equation for the electron energy distribution function (e.d.f.) [4-8]. In implicit form one can write :

$$\frac{dN_2(V)}{dt} = \left(\frac{dN_2(V)}{dt} \right)_{e-v} + \left(\frac{dN_2(V)}{dt} \right)_{e-D} + \left(\frac{dN_2(V)}{dt} \right)_{v-v} + \left(\frac{dN_2(V)}{dt} \right)_{v-T} \quad (1)$$

with $0 \leq V \leq 46$.

$$\frac{\partial n(u, t)}{\partial t} = - \frac{\partial J}{\partial u} + \text{In.} + \text{Sup.} + \text{Rot.} \quad (2)$$

where $n(u, t) du$ is the number of electrons with energy between u and $u + du$ and the right hand terms of equation (2) refer in the order to the flux of electrons along the energy axis and to the applied field and elastic collisions ($\partial J/\partial u$), to inelastic (In.), superelastic (Sup.) and rotational (Rot.) collisions. Calculated e.d.f. are given in reference [8] at different E/n (E electric field, n neutral density) with $E/n = (3-60) \times 10^{-16}$ V.cm², residence times ($t = 0$ to 10^{-1} s) and electron densities ($n_e = 10^{10}$ - 10^{11} cm⁻³) values.

The relaxation terms appearing in equation (1) refer to electron vibrational excitation (e-V), dissociation (e-D), vibration-vibration (V-V) and vibra-

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tion-translation (V-T) inelastic and superelastic processes. The inelastic processes are characterized by the following kinetic equations :

where $k_{V,W}^e$, k_d^e , $P_{V,0}^{W-1,W}$, $P_{V,V-1}^{W-1,W}$ and $P_{V,V-1}$ are the rate coefficients for electronic excitation, dissociation, non-resonant and near-resonant (V-V) exchanges and (V-T) exchanges. The relevant rate coefficients have been calculated in references [7-8] with the self-consistent e.d.f. for reactions (3-4) and by using [7] a semiclassical method for the cross sections of reactions (6-7).

The superelastic processes are deduced by using the following Boltzmann equilibrium relations :

$$\begin{aligned} k_{W,V}^e &= k_{V,W}^e \exp\left(\frac{\Delta E_{V,W}}{kT_e}\right), \\ P_{V-1,V} &= P_{V,V-1} \exp\left(\frac{\Delta E_{V-1,V}}{kT_g}\right), \\ P_{V-1,V}^{W-1,W} &= P_{V,V-1}^{W-1,W} \exp\left(\frac{2\delta \Delta E_{10}}{kT_g}\right) \end{aligned} \quad (8)$$

where δ is the anharmonicity constant, T_e and T_g are the electron and neutral temperatures and ΔE are the energy gaps.

It has been found that the $P_{V,V-1}$ rate coefficients are of three order of magnitude lower than the (V-V) exchange rates for $V < 20$. So these are the (V-V) processes which propagate the vibrational quanta introduced by the electron-collisions.

The strength of the vibrational excitation can be characterized by the value of the θ_1 temperature :

$$\theta_1 = \frac{\Delta E_{10}}{\text{Log } n_0/n_1} \quad (9)$$

where ΔE_{10} is the energy gap between $N_2(X, 1)$ of population n_1 and $N_2(X, 0)$ of population n_0 . Time variations of the n_1 , n_0 vibrational densities are given by equation (1).

Variations of θ_1 with the residence time (t) in the discharge are represented in figure 1 for the following parameters : $E/n = 3-6 \times 10^{-16} \text{ V.cm}^2$, $n_e = 10^{11}-10^{12} \text{ cm}^{-3}$, $T_g = 500 \text{ K}$ and $p = 5 \text{ torr}$ ($n \sim 10^{17} \text{ cm}^{-3}$). Are also indicated in figure 1 the values of the two following characteristic times :

$$i) \quad \tau_{e,v} = \frac{1}{n_e k_{1,0}^e} \quad (10)$$

Fig. 1. — Time variation of the θ_1 temperature $\left(\theta_1 = \frac{\Delta E_{10}}{\text{Log } n_0/n_1}\right)$ for several experimental conditions. Characteristic times for electron excitation ($\tau_{e,v}$) and V-V resonant exchange ($\tau_{v,v}$) are also indicated.

for electron deexcitation

$$ii) \quad \tau_{v,v} = \frac{1}{n_0 k_{1,0}^{0,1}} \quad (11)$$

for V-V resonant exchange process. The characteristic time for V-T processes are too high ($\sim 10^4 \text{ s}$) to be included in figure 1.

A highly excited vibrational distribution $N_2(X, V)$ will be obtained if the residence time (t) in the discharge is as long as $t > \tau_{e,v}$ and $t > \tau_{v,v}$.

With the discharge parameters chosen, these conditions are satisfied for $t > 1.5 \times 10^{-3} \text{ s}$.

The calculated e.d.f. are shown in figure 2 for the two residence times $t = 1.5 \times 10^{-4} \text{ s}$ and $t = 1.5 \times 10^{-3} \text{ s}$. The electron density in the high energy tail of the e.d.f. is increasing with the residence time. This effect is due to the electron heating by superelastic $e - N_2(X, V)$ collisions [8]. One can also mention that the N atoms production is also increasing with the residence time : $[N]/[N_2] \sim 10^{-4}$ at $t = 1.5 \times 10^{-4} \text{ s}$ and $\sim 1.5 \%$ at $t = 1.5 \times 10^{-3} \text{ s}$ for $E/n = 6 \times 10^{-16} \text{ V.cm}^2$ and $n_e = 10^{12} \text{ cm}^{-3}$. Large N atom concentration reduces the high energy tail of the electron energy distribution function by introducing new inelastic processes [8].

Vibrational distributions of $N_2(X, V)$ are represented in figures 3a, b in full lines for a residence time $t \sim 1 \text{ ms}$ in the discharge.

It can be noted that the high vibrationally excited levels $N_2(X, V)$ increase with E/n just like the e.d.f.

3. Vibrational distribution relaxation in post-discharges. — Relaxation of the $N_2(X, V)$ distribution has been calculated by eliminating the electron collisions at the end of the electrical discharge since it has been found that superelastic collisions can be

Fig. 2. — Calculated electron distribution functions for two residence times and two E/n values.

neglected. Results are shown in figures 3a, b for relaxation times smaller than 10^{-2} s. The parameters (E/n , n_e and p) of the initial discharge have been chosen in order to reproduce the θ_1 characteristic temperatures (cf. reaction (9)) experimentally found in a N_2 flowing afterglow discharge [3].

It can be seen in figures 3a, b that an overpopulation of high levels is obtained as the result of an efficient V-V pumping up effect. As for the low vibrational levels they are quickly depopulated when the electron excitation is disappearing. Our results are in agreement with the calculation of Hsu and McMillen [9] at $\theta_1 = 2\,500$ K and $T_g = 500$ K. From their study it can be deduced that when starting with a Boltzmann vibrational temperature at $\Delta t = 0$ the high levels are quickly overpopulated after a relaxation time of 10^{-5} to 10^{-4} s — an overpopulation which increases with time until a plateau is reached at $\Delta t \sim 10^{-2}$ s.

Since the deactivation on the discharge tube walls is not considered in the present calculation our investigation has been limited to relatively short relaxation times. The upper limit $\Delta t \sim 10^{-2}$ s has been chosen as being nearly the relaxation time for deexcitation of a vibrational level colliding with the tube wall [10].

It can be concluded from the calculated vibrational distributions shown in figures 3a, b that at a relaxation time $\Delta t = 3$ ms, the vibrational temperature θ_1 slightly increases by 12 % from its initial value $\theta_1^0 \sim 2\,000$ K but decreases by 12 % for

Fig. 3. — $N_2(X, V)$ vibrational distribution in the discharge at a residence time $t = 10^{-3}$ s and for several times in the post-discharge ($\Delta t = 1.3\text{--}5 \times 10^{-3}$ s). Figure 3a for $\theta_1 = 2\,000$ K, $4\,400$ K and figure 3b for $\theta_1 = 6\,800$ K.

$\theta_1^0 \sim 4\,400$ K and by 43 % for $\theta_1^0 \sim 8\,500$ K. Consequently the experimental value of the characteristic temperature « T_v » $\sim 8\,000$ K found in the flowing

afterglow experiment [3] at a transit time $\Delta t \sim 1\text{-}2$ ms appears to underestimate the characteristic temperature in the discharge. The two other temperatures « T_v » = 4 600 K and 2 800 K experimentally found [3] are likely a good value for the vibrational temperatures in the discharge.

4. Conclusion. — The electron and vibrational distribution functions have been calculated for time varying N_2 electrical discharges in the following experimental conditions : $p = 5$ torr, $T_g = 500$ K, $n_e = 10^{11}\text{-}10^{12}$ cm $^{-3}$, $E/n = 3\text{-}6 \times 10^{-16}$ V.cm 2 , residence times $t = 10^{-4}\text{-}10^{-3}$ s.

In the discharge, the electrons and vibrational species get overpopulated in the tails of their distribution functions. These overpopulations are mainly due to the superelastic vibrational collisions $e - N_2(X, V)$ for the electron distribution and to V-V transfers for the $N_2(X, V)$ distribution. These two distribution functions are coupled through inelastic and superelastic vibrational electron collisions.

In the post-discharge the vibrational distribution quickly varies with time, showing a depopulation of low levels and an overpopulation of high levels. The speed of this perturbation increases with the initial value of the vibrational temperature.

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