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Influence of superelastic vibrational collisions on the relaxation of the electron energy distribution function in N_2 post discharge regimes (*)

M. Capitelli, C. Gorse and A. Ricard (**)

Centro di Studio per la Chimica dei Plasmi del C.N.R.,
Dipartimento di Chimica, Via Amendola 176, 70123 Bari, Italy

(**) Laboratoire de Physique des Gaz et des Plasmas, Université de Paris-Sud, 91405 Orsay, France

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Résumé. — Nous avons étudié la relaxation de la fonction de distribution en énergie des électrons (edf) dans une « post-décharge » d'azote en résolvant l'équation de Boltzmann privée du terme dû au champ électrique. Les résultats ont été obtenus en tenant compte ou de la présence des collisions vibrationnelles superélastiques ou de leur absence.

Dans le premier cas, la fonction de distribution en énergie des électrons tend vers des valeurs riches en électrons dans l'intervalle d'énergie 2-4 eV qui varient peu avec le temps, alors que, dans ce même intervalle, sans collisions vibrationnelles superélastiques, la fonction de distribution en énergie des électrons présente un creux.

Ce comportement se reflète sur les coefficients de vitesse des différents processus. En particulier, en présence des collisions vibrationnelles superélastiques, les coefficients de vitesse d'excitation vibrationnelle, et d'excitation des atomes métastables d'azote $N(^2P, ^2D)$ conservent des valeurs élevées, même dans le régime de « post-décharge ».

Abstract. — The relaxation of the electron energy distribution function (edf) in N_2 post discharge regime has been studied by solving the Boltzmann equation without the term due to the electric field.

The results have been obtained both in the presence and in the absence of superelastic vibrational collisions.

In the first case the electron energy distribution function relaxes toward nearly time independent values rich in electrons in the energy range 2-4 eV, while in the absence of superelastic vibrational collisions edf presents a hole in this energy range.

This behaviour is reflected on the rate coefficients of the different processes. In particular, in the presence of superelastic vibrational collisions, the rate coefficients of the vibrational excitation and of the excitation of the metastable nitrogen atoms $N(^2P, ^2D)$ can conserve high values also in the post discharge regime.

1. Introduction. — Post discharge regimes are commonly studied in connection with the elementary processes occurring in the afterglow. The usual approximation which is made in these regimes is that the electrons, due to the disappearance of the electric field, have not sufficient energy to excite the neutral particles. Consequently well defined processes have been studied under the assumption that the perturbation of electron collisions is of minor importance. So in taking active nitrogen as working gas, experiments in time varying afterglows have allowed specific mechanisms to be studied such as the dissociative

electron ion (N_2^+) recombination [1] and the diffusion of active species as the $N(^2D, ^2P)$ metastables [2].

Flowing afterglow experiments have given the vibrational $N_2(X, v)$ distributions [3, 4] and the N atom concentration [5], while recent calculations [6] have shown the relaxation of the vibrational $N_2(X, v)$ in the post discharge regime.

In this letter we consider the relaxation of the electron energy distribution function (edf) in the post discharge regime, by emphasizing the role of vibrationally excited N_2 molecules in affecting this relaxation. This study, which is complementary with our previous work [6], can be used to judge the approximation of neglecting electron collisions in the experiments previously mentioned.

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2. Method of calculation and results. — The relaxation of edf can be obtained by solving the time dependent Boltzmann equation which can be written as [7, 8]

$$\frac{\partial n}{\partial t} = -\frac{\partial J_f}{\partial \varepsilon} - \frac{\partial J_{el}}{\partial \varepsilon} + \text{In} + \text{Sup} + \text{Rot} \quad (1)$$

where $n(\varepsilon, t) d\varepsilon$ represents the number density of electrons with energy between ε and $\varepsilon + d\varepsilon$. The different terms on the right hand side of equation (1) represent respectively, the flux of electrons along the energy axis driven by the applied field ($\partial J_f / \partial \varepsilon$), by elastic ($\partial J_{el} / \partial \varepsilon$), inelastic (In), superelastic (Sup) and rotational (Rot) collisions. Explicit expressions can be found elsewhere [7, 8].

The temporal evolution of $n(\varepsilon, t)$ at the exit of the discharge is obtained by imposing $E/N = 0$ at $t = 0$. This is indeed an approximation, since the electric field can not drop suddenly to zero in the post discharge. As an initial distribution $n(\varepsilon, t = 0)$ we consider a stationary distribution obtained at the end of the discharge by solving the Boltzmann equation coupled to a set of vibrational master equations including the vibrational excitation and the dissociation process (see Refs. [6, 8] for details and for the list of the adopted cross sections). In particular the results reported in figure 1a, b are consistent with a reduced electric field $E/N = 6 \times 10^{-16} \text{ V.cm}^2$ and with a vibrational distribution obtained after a residence time of 1 ms in the discharge (see Fig. 3 of Ref. [8]). This vibrational distribution, which is characterized by a 0-1 vibrational temperature of approximately 8 500 K ⁽¹⁾, of course affects $n(\varepsilon, t)$ through the superelastic vibrational collisions also in the post discharge regime. A realistic calculation of edf in the post discharge should couple equation (1) with the vibrational kinetics as done in the discharge. To simplify the problem, however, we consider that the vibrational distribution N_v does not vary at least during the time necessary to $n(\varepsilon, t)$ to achieve nearly time independent values.

Let us consider first, the case where we neglect the presence of vibrationally excited molecules (i.e. we drop the term Sup in Eq. (1)). Figure 1a reports the corresponding evolution of edf, which is in qualitative agreement with the results of reference [9]. It is interesting to note the lack of electrons with energy between 2-4 eV when the superelastic collisions are neglected. This is due to the difficulty met by the high energy electrons to penetrate the vibrational barrier of the 0-1 transition. A hole in edf in the energy range 2-4 eV is created, which is filled by the superelastic collisions in figure 1b. This figure in fact, reports the temporal evolution of edf under the presence of superelastic vibrational collisions. One can note that the electrons tend to concentrate themselves in the low energy portion of edf, reaching nearly time independent values in a time of the order of $7 \times 10^{-7} \text{ s}$. It should be

Fig. 1. — Temporal evolution of the electron energy distribution function $f(\varepsilon, t) = n(\varepsilon, t) \left[\frac{4\pi}{m_e} \left(\frac{2}{m_e} \right)^{1/2} \varepsilon^{1/2} \right]^{-1}$ [8] passing from $E/N = 6 \times 10^{-16} \text{ V.cm}^2$ to $E/N = 0$, calculated without (Fig. 1a) and with (Fig. 1b) superelastic vibrational collisions.

also noted that in the early stage of the evolution the electron energy distribution function presents high values in the energy range 5-7 eV.

The role of vibrational energy losses in affecting the temporal evolution of edf can be better understood from figure 2 where we have compared the edf of figure 1a at $t = 10^{-7} \text{ s}$ with the corresponding results obtained by neglecting the vibrational energy losses.

Fig. 2. — Different approximations to the electron energy distribution function of figure 1a at $t = 10^{-7} \text{ s}$ (dashed line : initial distribution at $t = 0$; curve 1 : complete calculations; curve 2 : calculations without vibrational inelastic losses; curve 3 : calculations without electronic energy losses; curve 4 : calculations without electronic and dissociation energy losses. See text.)

⁽¹⁾ This value has been experimentally found in flowing afterglow experiments [4].

We can see that also in this case the vibrational hole disappears. It should be also noted that the structure of edf in the energy range 2-4 eV approximately follows the structure of 0-1 electron vibration cross section. Two other interesting situations have been reported in figure 2 ; one which shows edf calculated by inserting only the vibrational energy losses and the dissociation process, the other one which shows edf calculated by neglecting all electronic energy losses including the dissociation process. The corresponding results once again show the importance of the vibrational energy losses in affecting edf in the 2-6 energy range.

The electronic energy losses affect edf in the high energy tail $\varepsilon > 6$ eV. This last result is correlated with excitation of the N₂(A ³Σ_u⁺) metastable state (threshold 6 eV), dissociation (about 10 eV) and ionization (14.6 eV).

The edf hump around 6 eV reflects the absence of inelastic processes which characterizes the nitrogen molecule.

Fig. 3. — Temporal evolution of the electron energy distribution function passing from $E/N = 3 \times 10^{-16}$ V.cm² to $E/N = 0$ (a, b as in figure 1).

Figure 3a, b shows the temporal evolution of edf in the post discharge regime, starting at $t = 0$ with an edf consistent with an $E/N = 3 \times 10^{-16}$ V.cm² and a vibrational distribution characterized by a 0-1 vibrational temperature of 3 400 K as found in [4]. The results obtained in the absence (Fig. 3a) and in the presence (Fig. 3b) of superelastic vibrational collisions follow those discussed in figure 1a, b.

Let us now consider the evolution of selected rate coefficients. We can expect that the rate coefficients for inelastic processes having low energy thresholds E_s can conserve appreciable values during the temporal evolution of edf in the post discharge, while processes having high energy thresholds will present rate coefficients strongly decreasing with time. This is

indeed the case as one can appreciate from figures 4-5, a-b where the rate coefficients for the following processes

have been reported as a function of time.

Fig. 4. — Rate coefficients as a function of time for selected processes (a, b as in figure 1) :

1. $e + N_2(v = 0) \rightarrow e + N_2(v = 1)$
2. $e + N(^4S) \rightarrow e + N(^2D)$
3. $e + N(^4S) \rightarrow e + N(^2P)$
4. $e + N_2 \rightarrow e + N_2(A ^3\Sigma_u^+)$
5. $e + N_2 \rightarrow e + N_2(B ^3\Pi_g)$
6. $e + N_2 \rightarrow e + N_2(C ^3\Pi_u)$

Fig. 5. — Rate coefficients as a function of time for selected processes as in figure 4a, b.

Once more the behaviour of the rate coefficients obtained with the insertion of superelastic vibrational collisions (see Figs. 4-5-b) is completely different from that obtained by neglecting those collisions. In parti-

cular one notices that the rate coefficients for processes (a), (b) conserve appreciable values when the superelastic vibrational collisions are retained in the equations.

The effect of superelastic vibrational collisions is less pronounced with $\theta_1 = 3\,400$ K (Fig. 5) since for this situation the $N_2(X, v)$ vibrational distribution is less overpopulated at $t = 0$ than with $\theta_1 = 8\,400$ K (see [6]).

3. Conclusions. — The results reported in the present letter show that at the exit of a nitrogen flowing discharge, the presence of vibrationally excited molecules can maintain nearly time independent electron energy distribution functions with appreciable populations in the energy range 2-5 eV. This situation is particularly reflected on the rate coefficients which depend on this part of edf. In particular the vibrational excitation of the first few levels as well as the excitation of metastable states of atomic nitrogen can be still effective in the post discharge regime, thereby affecting the results reported in references [2, 6].

It is very difficult to estimate the importance of this behaviour on both situations. A correct solution of the problem should require the coupling in the post discharge regime of the Boltzmann equation with the system of vibrational master equations including the dissociation and ionization processes and the continuity equation for the electron density. This is indeed a very difficult problem, the solution of which is beyond the aim of this letter.

It is sufficient to say here that the results of reference [6] on the evolution of N_v distribution underestimate the vibrational temperature of the first few levels since the electron-vibration energy exchanges can be effective also in the post discharge. The introduced error should not exceed a few percent since the electron-vibration rates decrease passing from the end of the discharge to the post discharge regime.

Similar conclusions can be made on the excitation of metastable nitrogen atoms [2], even though in this case the formation of nitrogen atoms as a result of the V-V (vibration-vibration) pumping up mechanism [8] can further complicate the situation.

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