SELF-CONSISTENT ELECTRON ENERGY AND VIBRATIONAL DISTRIBUTION FUNCTIONS
IN STATIONARY NITROGEN DISCHARGES

J. Loureiro and C.M. Ferreira
Centro de Electrodinâmica, Instituto Superior Técnico,
1096 Lisboa Codex, Portugal

ABSTRACT

We present self-consistent calculations of electron energy distribution functions, rate coefficients and transport parameters, of vibrational distribution functions of \( N_2(X) \) molecules, and of the rate of dissociation for typical conditions of a stationary discharge in \( N_2 \) at low pressures. A relationship between the characteristic vibrational temperature, \( \theta \), and the discharge parameters \( E/N \) and \( n_e/N \) is obtained. The power balance in the discharge is analysed in detail.

1. INTRODUCTION

The superelastic collisions of the electrons with vibrationally excited molecules in the electronic ground state, \( N_2(X \Sigma_g^+) \), are known (1) to affect strongly the electron energy distribution function (EDF) in a discharge and to play, therefore, an important role in the discharge kinetics. In particular, the production of nitrogen active species of interest for, e.g., gas lasers and plasma chemistry applications, is strongly influenced by these mechanisms.

In the last few years, the problem of the time evolution of the coupled EDF's and vibrational distribution functions (VDF's) in \( N_2 \) has been analysed by various authors (2) using a self-consistent approach based on solutions to the coupled system of the electron Boltzmann equation and the vibrational master equations. Analyses of this type for steady-state conditions are not, however, available from the literature making it difficult to interpret experiments conducted on stationary discharges such as those reported in (3). In particular, it seems useful to obtain information on the EDF's, the VDF's, the electron transport parameters and excitation rates, the rate of dissociation and the power transfer as a function of similarity parameters characterizing the discharge operating conditions. This constitutes the basic purpose of this work.

2. THEORETICAL FORMULATION

We have used and solved simultaneously the steady-state, homogeneous Boltzmann equation, as derived from the usual two-term expansion approximation (4), and the system of steady-state rate balance equations for the vibrational levels of \( N_2(X) \) including e-V, V-V, and V-T energy exchange processes. The superelastic e-V collisions were taken into account both in the Boltzmann and in the rate balance equations. Superelastic collisions
of the electrons with electronically excited molecules were, however, neglected. Moreover, the excitation of electronic states by electron collisions was treated as a single-energy loss process. Under these assumptions the Boltzmann equation may be written

\[
\frac{d}{du} \frac{E}{N} \left( \frac{1}{3} \right) \frac{2}{u} \frac{df}{du} + \frac{2m}{M} \sigma_c \frac{u^2}{e} \left( f + \frac{K T_e}{e} \frac{df}{du} \right) + 4B \sigma_o \frac{uf}{e} = J_e(f) + J_v(f),
\]

(1)

where

\[
J_e(f) = \sum Y \left[ uf(u) \sigma Y(u) - (u + V_Y) f(u + V_Y) \sigma Y(u + V_Y) \right]
\]

(2)

accounts for the excitation of the electronic states N_2(Y) from N_2(X) (\sigma_Y and V_Y denoting the corresponding cross section and energy threshold), and

\[
J_v(f) = \sum Y \sigma \left[ uf(u) \sigma Y'+(u-(u+V_{vv})f(u+V_{vv})\sigma Y'+(u+V_{vv})\right] +
\]

\[
\sum Y \sigma Y \left[ uf(u) \sigma Y'(u) - (u-V_{vv}) f(u-V_{vv}) \sigma Y'(u-V_{vv}) \right]
\]

(3)

accounts for the inelastic (cross sections: \sigma Y') and superelastic (cross sections: \sigma Y) e-V energy exchanges. Here, \delta_Y = N_Y/N is the fractional population in the v-th level, f(u) is the EDF with the normalisation \int_0^\infty f u^{1/2} du = 1, u = mv^2/2e is the electron energy in eV, \sigma_c is the momentum transfer cross section, T_e is the gas temperature in Kelvin, B = 2.5 \times 10^{-6} eV is the rotational constant for N_2, and \sigma_o = 8\pi q^2 a_o^2/15, where q = 1.601 is the electric quadrupole moment in units of e \cdot \alpha^2.

Eq. (1) is coupled through the \delta_Y's to the system of 46 rate balance equations for the vibrational levels. These equations are of the type

\[
\frac{dN_v}{dt} e-V + \frac{dN_v}{dt} V-V + \frac{dN_v}{dt} V-T + R_v = 0
\]

(4)

where the dN_v/dt terms account for the e-V, V-V and V-T processes (their explicit form may be found in Ref. 2), and R_v is the rate of recombination into the v-th level. Only single quantum V-V and V-T transitions, which are the most likely ones, were considered. Dissociation by these processes was taken into account assuming that it corresponds to a transition to a pseudolevel above the last vibrational level (v=45). Under steady-state conditions, v R_v must compensate exactly for the total dissociation rate, v d, this condition insuring that the Eqs. (4) are linearly dependent and have an unique solution satisfying the normalisation condition \sum Y \delta_Y = 1. We have assumed that R_v = v_d v with v_r = 1, and have worked out calculations making different assumptions about the distribution r_v. The results shown below are for the case r_0 = 1, r_v = 0 for v > 0. Using other assumptions causes negligible changes in the VDF at low v-levels.

Eqs. (1) and (4) determine the EDF and the VDF as a function of the independent parameters E/N and \delta = n_e/N (degree of ionisation), thereby providing fundamental similarity laws for the steady-state problem.

The basic electron cross sections used are the set developed by Pitchford and Phelps (5) from transport and scattering data. The cross sections for the X_v+X_w+v transitions were assumed identical in shape and magnitude to the ones for the X_0+X_w+v transitions. The cross sections for the superelastic processes were obtained from detailed balancing.
The rate coefficients for the V-V and V-T processes have been calculated from the modified SSH theory (6) using the results reported in (7) and (8) for normalisation.

3. RESULTS

We define \( \theta \) as the characteristic vibrational temperature of the Treanor-like distribution (9) that best fits to the calculated VDF for the lowest four v-levels; \( \theta \) characterizes the degree of vibrational excitation and is a function of E/N and \( \delta_e \).

Figs. 1a and 1b show the EDF and the VDF for E/N=10^{-15}Vcm^{-2} and various values of \( \theta \). The VDF's are approximately Treanor-like distributions at low v-levels but, with increasing v, there appears a slowly decreasing region followed by a steeply decreasing one near the dissociation limit. This shape is caused here by the propagation of the dissociation effects down the vibrational ladder and not by the near-resonant V-V and the V-T exchanges like in CO(10).

Fig. 2 shows curves of \( \delta_e \) vs. E/N for various constant values of \( \theta \). The data points represent values of \( \delta_e \) and E/N in the experiments reported in (3) for the pressures of 0.1, 0.7, and 1 Torr and the currents of 5, 20 and 50mA.

Fig. 3 shows the electron rate coefficients for the excitation of the A \( ^3\Sigma^+ \) and the B \( ^3\Pi \) states vs. E/N for various values of \( \theta \). At the lower E/N values these rate coefficients become much larger, as \( \theta \) increases, than those calculated in the absence of vibrational excitation, i.e., for \( \theta=0 \).

Fig. 4 shows the rate of dissociation per molecule at unit gas density, by the V-V and the V-T processes and by electron collisions, vs. \( \theta \) for E/N=10^{-15}Vcm^{-2}.

Fig. 5 shows curves of the power transferred per molecule at unit gas density to the coupled translational-rotational modes by the V-T (A1) and the nonresonant V-V (A2) energy exchanges and by electron collisions (B) vs. \( \theta \) for E/N=10^{-15}Vcm^{-2}.

Calculations of other relevant quantities were carried out as well and will be made available at the conference.

REFERENCES

(3) Cernogora, G., C.M. Ferreira, L. Hochard, M. Touzeau, and J. Loureiro,
Figure 1. EDF's (a) and VDF's (b) for $E/N=10^{-15}\text{ Vcm}^{-2}$ and the following values of $\theta$ in $10^3\text{K}$: 2(A), 3(B), 4(C) and 6(D).

Figure 2. $\delta_e$ vs. $E/N$ for the values of $\theta$ in $10^3\text{K}$: 6(A), 4(B), 3.5(C), 3(D) and 2(E). Data points of $\delta_e$ and $E/N$ in a glow discharge for the values of $p$ in Torr: 0.1(Δ), 0.7(O) and 1(□) and for the values of $I$ in mA: 5(lower), 20 (intermediate) and 50(upper points).

Figure 3. Electron rate coefficients for the states $A^{3\Sigma_u^+}$ (full curves) and $B^{3\Pi_g}$ (dashed curves) vs. $E/N$ and for the values of $\theta$ in $10^3\text{K}$: 0(A), 2(B), 4(C) and 6(D).
Figure 4. Rate of dissociation per molecule at unit gas density by V-V and V-T processes (A) and by electron collisions (B) vs. $\theta$ for $E/N=10^{-15}$ V cm$^{-2}$.

Figure 5. Power transferred to the T-R modes per molecule at unit gas density by V-T ($A_1$) and nonresonant V-V ($A_2$) processes (curve A is the sum of $A_1$ and $A_2$) and by electron collisions (B) vs. $\theta$ for $E/N=10^{-15}$ V cm$^{-2}$. 

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