ELECTRON ENERGY DISTRIBUTION FUNCTION IN THE AFTERGLOW OF A MICROWAVE DISCHARGE IN FLOWING NITROGEN

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Abstract

In the context of the study of the so-called Short-Lived Afterglow (SLA) [1,2], a secondary ionisation zone arising in the afterglow of flowing nitrogen discharges, triple probe technique [3] has been applied to study the local electron population in this medium. Parallely to experiments, a model for the electron energy relaxation allowing to calculate the Electron Energy Distribution Function (EEDF) and the electron density in the SLA has been developed.

1. Introduction

In recent years, large interest has been devoted to the study of flowing N₂ post-discharges mainly motivated by pressing problems with great impact in applications related to surface treatments, such as dissociation of nitrogen. This fact has motivated the appearing of several spectroscopic studies of the most intense emission bands of N₂ and N₂⁺. In particular, it has been observed that flowing N₂ discharges produce the so-called pink afterglow, where the emission bands of the first negative system of N₂, associated with the transition N₂⁺(B → X), and of the first positive system, associated with the transition N₂(2Π → 2Σ), grow up in the afterglow after a dark zone positioned at the end of the discharge [4,5]. This behaviour for N₂(B) and N₂⁺(B) is analysed in another contribution to this conference [6]. Here we will study the relaxation of the Electron Energy Distribution Function (EEDF) and of the electron density in the Short-Lived Afterglow (SLA) of a microwave flowing nitrogen discharge. It will be shown that the profile of the electron density in the SLA initially decreases, as a consequences of electron losses by ambipolar diffusion and electron-ion recombination, but later on it exhibits a pronounced maximum due to the creation of new electrons from associative ionization.

2. Experiment

EEDFs were deduced from second derivatives of digitized probe characteristics measured using a triple probe technique.
In this experiment, a tungsten wire of 3 mm length and 50 μm radius forms the probe tip. The probe is supported by a glass capillary tube covered by a partially insulated stainless steel tube whose exposed region plays the role of auxiliary electrode. In order to minimize plasma and flow perturbations, the reference electrode was chosen to be an emissive one [7] and it was inserted downstream into the discharge tube while the probe enters radially through a PTFE sleeve which enables its radial movement under vacuum. Electrically, the active probe is connected to the input of a transimpedance amplifier (virtual ground) through a second order, anti-aliasing filter which also provides regularization without needing to record many probe characteristics in a systematic way. The sweeping potential is applied to the reference electrode. A PC based data acquisition board digitizes the auxiliary electrode potential and the output from the above amplifier. Since an oscilloscope’s analysis of the probe floating potential did not show any fluctuations at frequencies above the anti-aliasing filter cut-off, there was no need for probe compensation. Both the probe arrangement used here and the numerical differentiation scheme (Hamming apparatus function with an adaptive size) are similar to those described in [8].

The measured potentials were corrected for a non-negligible sheath impedance, as compared to the finite input impedance of the data acquisition board, which arises at low electron densities. In this line, the active probe and the auxiliary electrode role were interchanged and two sets of V-I characteristics were measured from which the sheath impedances were derived.

As it is known [9], the second derivative of the probe characteristics is not EEDF representative when the electron free path and the probe radius are of the same order of magnitude. Mathematically speaking, to deduce the EEDF from probe measurements under collisional conditions requires that two coupled inverse problems are solved, since the distortion of the second derivative includes an integral over the unknown EEDF and the data are convoluted by the apparatus function. The situation is simpler when the EEDF can be assumed Maxwellian. Then, the problem solution requires only two unknown parameters, the electron density and temperature, which can be used as fitting parameters through a comparison between measured and theoretical probe characteristics [10]. However, under our experimental conditions, the probe current is clearly distorted by collisions (the mean free path is about twice the probe radius) and the assumption of a Maxwellian EEDF constitutes a rough approximation. So, we felt the need to devise a method to correct for the collisional effects on the second derivative of the probe characteristics. Basically, the theoretical probe characteristic [9] corresponding to a seeded EEDF is compared against the measured one and corrections are iteratively introduced in the EEDF until an acceptable matching is achieved. Details of this method will be presented at the conference.
2. Theory

To interpret the experiments, a theoretical model for the electron energy relaxation, allowing to calculate the Electron Energy Distribution Function (EEDF) and the electron density in the SLA, has been developed. First, the EEDF in the discharge is obtained by solving the Boltzmann equation, under the effective field approximation, coupled to a system of rate balance equations for the vibrational and electronic states of N\(_2\), N(4S) atoms and N\(_2^+\) and N\(_4^+\) ions, in which the sustaining electric field is self-consistently determined [11]. Once the EEDF in the discharge is obtained, the EEDF in the post-discharge is calculated by solving the time-dependent Boltzmann equation using the stationary distribution in the discharge as initial condition, assuming zero electric field and a continuous transition from ambipolar to free diffusion regimes resulting from the diminution of the space-charge field [12].

In order to explain the maximum of the electron density in the SLA after a dark zone, the creation of new electrons has also been accounted for in the Boltzmann equation. The following ionization mechanisms have been included as sources of electrons in the post discharge:

\[
N_2(A) + N_2(a') \rightarrow N_2^+ + N_2 + e \quad (1)
\]

\[
N_2(a') + N_2(a') \rightarrow N_2^+ + N_2 + e \quad (2)
\]

\[
N_2(X, v \geq 30) + N_2(a') \rightarrow N_2^+ + N_2 + e \quad (3)
\]

and

\[
N_2(X, v \geq 36) + N_2(B) \rightarrow N_2^+ + N_2 + e \quad (4)
\]

The concentrations \([N_2(A)]\), \([N_2(B)]\), \([N_2(a')]\) and \([N_2(X, v \geq 30)]\) in the post-discharge were calculated using a detailed kinetic model for the heavy-particles in a nitrogen afterglow for the same conditions used here [6,11], and were introduced in the Boltzmann equation. However, notice that the vibrational temperature of the lower levels of the vibrational distribution function (VDF) of \(N_2(X^1\Sigma_g^+)^\) molecules was kept constant in the Boltzmann equation for the afterglow. Reactions (3) and (4) are negligible under discharge conditions, since the high vibrational levels of ground state \(N_2\) molecules are efficiently destroyed in \(V-T\) collisions with nitrogen atoms. Nevertheless, the tail of the VDF passes through maximum in the afterglow at \(t \sim 10^{-3} - 10^{-2}\) s, since the near-resonant \(V-V\) energy exchanges produce a climbing of the vibrational ladder for quanta at the higher \(v\) levels (the so-called \(V-V\) pumping up effect) [6,11]. Therefore, processes (3) and (4) constitute an important source of electrons in the post-discharge.

3. Results and discussion

The experiments and the calculations were carried out for typical operating conditions of a flowing microwave discharge in pure \(N_2\). In particular, the field frequency was \(\omega/(2\pi) = \)
433 MHz, the pressure was \( p = 3.3 \) Torr, and the discharge was made on a quartz tube with inner radius \( R = 1.9 \) cm. The calculated electron density in the beginning of the afterglow was \( n_e \sim 1.9 \times 10^{11} \text{ cm}^{-3} \).

Fig. 1 shows the EEDF calculated at different instants (\( t = 0 - 1 \times 10^{-4} \text{s} \)) in the afterglow of a microwave discharge in nitrogen. This figure shows that a rapid depletion of the high-energy tail of the EEDF takes place at the earlier instants of the afterglow (\( t < 10^{-7} \text{s} \)) as a result of inelastic electron collisions. However, the electron density remains relatively high up to much longer times. The EEDF is calculated in the presence of \( e-e \) collisions, since during the relaxation process the EEDF goes towards the low-energy part of the distribution, where the Coulomb cross section, which sharply increases with decreasing electron energy, plays an important role in affecting the EEDF.

Fig. 2 shows the measured and calculated values for the electron density in the afterglow. The measurements made by interferometry in [13] are also plotted for comparison. The dashed curves correspond to the calculations made including only processes (1) and (2) as sources of electrons in the post-discharge [11], whereas on the full curves the processes (3) and (4) were also taken into account, with \( k_3 = 10^{-14} \text{ cm}^3 \text{s}^{-1} \) and \( k_4 = 10^{-11} \text{ cm}^3 \text{s}^{-1} \). There is a reasonable quantitative agreement between calculations and experiments. This choice of coefficients was dictated by the comparison between calculated and measured profiles of \( n_e \). An increasing in \( k_3 \) would lead to a broadening of the peak, since in order to obtain a narrow peak only collisions of \( N_2(X,v) \) molecules in high levels, typically \( v > 35 \), should be involved. It is observed that the electron density \( n_e \) initially decreases, but later on has a pronounced increase, passing through a maximum. This maximum of the electron density follows the maxima of the concentrations of the heavy species \( N_2(4), N_2(5), N_2(a') \) and \( N_2(X,v \geq 30) \) [6], and it is hence a direct consequence of reactions (1-4). Details on the kinetics of the heavy-species can be found in another paper to this conference [6].

Fig. 3 shows the EEDF’s measured at the discharge axis for different axial positions. The shape on the EEDF on the range of energies \( u < 4 \) eV is a consequence of the quasistationary state achieved between EEDF and VDF, in which the superelastic collisions of electrons with vibrationally excited molecules \( N_2(X,v) \) compensate for the inelastic vibrational losses, and reflects, therefore, the vibrational temperature \( T_v(N_2) \) of \( N_2(X,v) \) molecules. As it can be seen from this figure, \( T_v(N_2) \) does not change appreciably in this region of the afterglow. This is in agreement with the calculations made in [6] and shows that the assumption of a constant vibrational temperature in the afterglow for the Bottlman calculations is acceptable.

Fig. 4 shows the comparison between calculated and measured EEDFs in the post-discharge for a distance from the launcher \( Z \sim 12.5 \) cm. This figure shows that the vibrational temperature of the lower levels of the VDF calculated at the end of the discharge is probably overestimated, which may be caused by an overestimation of the electron density.
Fig. 1: EEDF calculated at different instants

Fig. 2: Electron density in the afterglow. (■) probe and (○) interferometry measurements; (—) calculations including reactions (1-4) and (—) reactions (1) and (2) only

Fig. 3: EEDF measured at different axial positions

Fig. 4: EEDF measured (■) and calculated (—) at $Z = 12.5$ cm

at the beginning of the afterglow.

Finally, figs. 5 and 6 show the radial profiles of the electron density and of the
4. Conclusions

The Electron Energy Distribution Function and the electron density were measured in a nitrogen afterglow by means of a triple probe technique. The experimental measurements were compared with the results of a detailed kinetic model for the post-discharge. It is shown that the electron density has a narrow peak in the afterglow, which is attributed to the creation of new electrons in the reactions $N_2(X, r \geq 30) + N_2(u') \rightarrow N_2^+ + N_2$ and $N_2(X, r \geq 30) + N_2(B) \rightarrow N_2^+ + N_2$. The tail of the Vibrational Distribution Function of $N_2(X^{1S_a})$ molecules passes through a maximum at $t \sim 10^{-3} - 10^{-2}$ s due to V-V pumping up and plays a central role in the whole problem.

References