Determination of $N_2(X,v)$ densities in the plasmas and afterglows of $Ar - N_2$ microwave discharges

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The $N_2(X,v)$ vibrational densities are determined in $Ar - xN_2$ flowing microwave plasmas and afterglows with x = 2-100% at 4 Torr, 1 slpm and 30-100 Watt from emission intensities of N_2-2nd and 1st pos. bands. In these plasma conditions, the θ_1–characteristic vibrational temperatures of $N_2(X,v)$ are found to be $6 - 10\ 10^3$ K for $x = 20 - 100\%$, corresponding to a density of $N_2(X, v > v_T = 5 - 6)$ of about $2\ 10^{16}\ cm^{-3}$ where v_T is the Treanor minimum. In the afterglow which follows at time of $3\ 10^{-3}$s, the density of $N_2(X, v > 13)$ varies from 1 to $5\ 10^{13}\ cm^{-3}$ for $x = 2 - 100\%$, that is one order of magnitude lower than the N-atom density.

1. Introduction

Afterglows of N_2 flowing microwave discharges have been studied at medium gas pressures (1-20 Torr) for sterilization of medical instruments by N-atoms [1,2]. It is studied the $Ar - x\%N_2$ gas mixtures with $x = 2 - 100\%$, to increase the electron energy in the plasma at constant values of transmitted power and of gas pressure. Superelastic collisions of electrons on the Ar metastable atoms produced in the plasma enhance the electron energy. The interest of $Ar - N_2$ gas mixture is also to maintain the plasma at high gas pressure, up to the atmospheric gas pressure while keeping a plasma power as low than 100 Watt [3].

The intensities emitted by the N_2 first positive (1st pos.) and N_2 second positive (2nd pos.) systems are measured to obtain the rotational and vibrational temperatures in the plasma and to determine the N-atom, the $N_2(A)$ and $N_2(X, v > 13)$ metastable molecules and the N_2^+ ion densities in the afterglow, after calibration by NO titration [4].

2. Experimental setup

The experimental setup is shown in **Fig.1**. A dia.5 mm discharge tube is directly connected to a 5 litre reactor. The $Ar - x\%N_2$ microwave plasmas are produced by a surfatron cavity at 2450 MHz, 30-100 Watt, 1 slpm and at a gas pressure of 4 Torr to allow a homogeneous diffusion of the afterglow inside the 5 litre reactor.

The plasma is located inside the dia.5 mm tube with a length after the surfatron gap varying from about 5 cm in pure N_2 to 20 cm in the Ar-2%N_2 gas mixture. With a discharge tube length of 30 cm after the surfatron gap, the residence time at the entrance of the 5 litres reactor is $3\ 10^{-3}$s.

The optical emission spectroscopy across the discharge tube and the 5 litre reactor is performed by means of an optical fiber connected to an Acton Spectra Pro 2500i spectrometer (grating 600 gr/mm) equipped with a Pixis 256E CCD detector (front illuminated 1024 x 256 pixels).

The plasma emission is recorded at the surfatron gap with a spatial resolution estimated to be 1 cm. The rotational temperature is measured from the rotational structure of the N_2 1st pos. at 775 nm [5]. The vibrational temperature in the plasma is deduced from the N_2 2nd pos. $\Delta v = -2$ vibrational sequence.

In the afterglow, the N–atom density is obtained from the N_2 1st pos. emission at 580 nm (I_{580}) after calibration by NO titration as described in [4]. The density of other active species of the afterglow such as $N_2(A)$ and $N_2(X, v > 13)$ molecules are obtained from the line intensity ratio method discussed in [6].

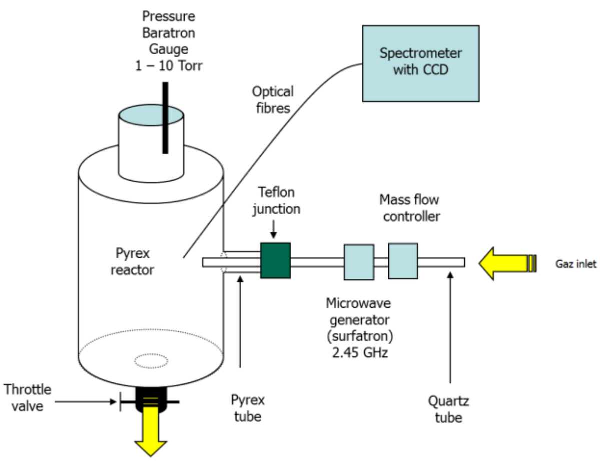

Fig.1 Microwave discharge and post-discharge reactor.

3. The Ar-N_2 plasma

3.1. Plasma gas temperature

As reported in [5], the intensity ratio (P_1/P_2) of the first two rotational sub-bands (labelled as P_1 and P_2) of the 1st pos N_2 band at 775 nm is related to the rotational temperature (T_R) of the plasma, which is usually between 300 and 1000 K. It is an important characteristic parameter of the N_2 plasma since it is directly related to the gas temperature due to the efficient rotational-translational energy transfer.

The gas temperature at the $Ar - x\%N_2$ HF plasma gap at 4 Torr is varying from 300-340 K at 30 Watt to 400 K at 50 Watt and 500 K at 100 Watt for $x = 2 - 100\%$.

3.2. Plasma vibrational temperature

The vibrational $T_v(C)$ and characteristic $\theta_1(X)$ temperatures, corresponding to the excited $N_2(C^3\Pi_u)$ and to the $N_2(X^1\Sigma_g^+)$ ground states, are determined following two steps.

First, it is considered the $f(v)$ vibrational distribution of $N_2(X,v)$ as given in [7]:

$$f(v) = f(0).\exp^{-v\left(\frac{E_{10}}{\theta_1(x)} - \frac{(v-1)E_{10}\delta}{Tg}\right)} \qquad (1)$$

with $f(0) = 1 - \exp^{-\frac{E_{10}}{\theta_1(x)}}$ for $v < v_T$, v_T being the vibrational number of the Treanor minimum with $v_T = \frac{T_g}{2\delta\theta_1(x)} + 0.5$, $E_{10} = E(X,1) - E(X,0)$ and δ anharmonicity constant. For N_2 (X), $E_{10} = 3396$ K and $\delta = 6.22\ 10^{-3}$.

The population of N_2(X,v) is written as: $[X,v] = f(v).N_0$ ($N_0 = N_2$ density).

Second, it is considered that the electron excitation from $[X,v]$ to $[C,v']$ follows the Franck-Condon principle (vertical direct excitation by electron collisions). The stationary $[C,v']$ population is then as follows :

$$[C,v'] = \Sigma_v[X,v]\ \upsilon_e(C)\ q(X,v\text{-}C,v')\ /\ \upsilon_l(C,v') \qquad (2)$$

where $q\ (X,v - C,v')$ is the Franck-Condon factor, $\upsilon_e(C)$ and $\upsilon_l(C,v')$ are the electron excitation and loss frequencies, with $\upsilon_l(C,v') = \upsilon_R(C,v') + N_0\ k_Q(C,v')$, $\upsilon_R(C,v')$ being the radiative loss frequency [8], and $k_Q(C,v')$ the collisional quenching rate by the N_2 molecules, that can be neglected in front of $v_R(C,v')$ for $p > 5\ Torr$.

The Boltzmann graphs of the vibrational $T_v(C)$ and characteristic $\theta_1(X)$ temperatures are represented in Fig.2 by normalizing the $N_2(C,v')$ population $[C,v' = 0] = 1$. As previously described [5], the experimental $[C,v' = 0 - 3]$ population is obtained by measuring the band head intensity of the N_2, 2nd pos. sequence $\Delta v = -2$.

From the curves in Fig.2, it is determined the following vibrational temperatures: $T_v(C) = 8\ 10^3$ K and $\theta_1(X) = 1\ 10^4$K in the N_2 plasma at 4 Torr, 1 slpm, 100 Watt.

With $T_g = 500$ K and $\theta_1(X) = 1\ 10^4$K, it is calculated a Treanor minimum: $v_T = 4$ and following (1) it comes $[X,v = 7] = 1.6\ 10^{16}cm^{-3}$.

At 50 W, it is found $T_v(C) = 7\ 10^3$K and $\theta_1(X) = 8\ 10^3$K. With $T_g = 400$ K and $\theta_1(X) = 8\ 10^3$K, it is calculated a Treanor minimum: $v_T = 4$ and $[X,v = 4] = 1.5\ 10^{16}cm^{-3}$ that is about the same value as at 100 W.

For the $Ar - 20\%N_2$ HF plasma, it is determined: $T_v(C) = 8\ 10^3$K and $\theta_1(X) = 8 - 10\ 10^3$K. With $T_g = 400$ K and $\theta_1(X) = 8\ 10^3$K, it is calculated a Treanor minimum: $v_T = 5 - 6$ and $[X,v = 5] = 2\ 10^{16}cm^{-3}$.

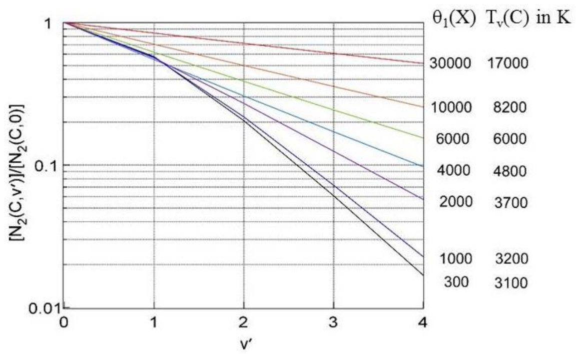

Fig.2 Vibrational distribution of the $N_2(C,v')$ vibrational states for several $T_v(C)$ and $\theta_1(X)$ at $T_g = 300$ K.

It is concluded that there is not a marked change of vibrational temperatures in the N_2 and $Ar - 20\%N_2$ plasmas: $\theta_1(X) = 8\ 10^3$K and the density of $N_2(X,v > v_T)$ with $v_T = 4 - 7$ of $1.5 - 2\ 10^{16}cm^{-3}$.

Lower vibrational temperatures were observed at low $\%N_2$ into Ar. With the $Ar - 2\%N_2$ gas mixture, it is determined: $T_v(C) = \theta_1(X) = 4 - 5\ 10^3$K at 30 W and $T_v(C) = \theta_1(X) = 6\ 10^3$K at 100 W.

With $T_g = 340$ K (500 K) at 30 W (100 W), it is calculated a common Treanor minimum: $v_T = 7$ and $[X,v = 7] = 5 - 6\ 10^{15}cm^{-3}$ that is 2 times lower than in N_2 and $Ar - 20\%N_2$ plasmas.

4. The Ar-N_2 afterglows

4.1. Afterglows characteristics

By emission spectroscopy, it is detected the N_2 1st pos. and N_2 2nd pos. in the afterglows at the entrance of the 5 liters reactor (see **Fig.1**), at time of $3\ 10^{-3}$s.

By analyzing the N_2 1st pos. vibrational distribution, it has been observed that the N_2 afterglow emission is a mixture of pink and late afterglow emission. The late afterglow contribution was evaluated through the calculation of the a_{N+N} factor [4].

It was found $a_{N+N} = 0.9$ for pure N_2 and $a_{N+N} = 0.75$ for the $Ar - 20\%N_2$ mixture in the 5 litre reactor. These results indicate an dominant part of the late afterglow contribution.

4.2. Densities of N, N_2(A) and N_2(X,v>13)

In the late afterglow, the N-atoms recombine as follows [4]:

$$N + N + N_2 \rightarrow N_2(B, 11) \rightarrow N_2(A, 7) + hv(580nm) \quad (a)$$

The I^m_{580} measured intensity of the N_2 580 nm band can therefore be used to monitor the variation of the square of the relative N-atom density. Absolute values were deduced after calibration by NO titration :

$$a_{N+N}\, I^m_{580} = k_3\, [N]^2 \qquad (3)$$

It is obtained a N-atom density in the 5 litre reactor of $5 - 6\ 10^{14} cm^{-3}$ in N_2 and $Ar - 20\%N_2$.

The $N_2(A)$ and $N_2(X, v > 13)$ densities were obtained by the line-ratio method as developed in [6].

For the $N_2(A)$ density determination, it is considered that the main reaction of $N_2(C)$ excitation is from the following pooling reaction:

$$N_2(A) + N_2(A) \rightarrow N_2(C) + N_2 \rightarrow N_2, 2^{nd}\ (316\ nm) \quad (b)$$

Then it is considered the following line–ratio:

$$a_{N+N}\, \frac{I^m_{580}}{I^m_{316}} = k_4 \left(\frac{[N]}{[N_2(A)]}\right)^2 \qquad (4)$$

The k_4 coefficient is calculated from the rate coefficients of reactions (a) and (b) as reported in [4,6].

It is found a constant $N_2(A)$ density between $10^{10} - 10^{11} cm^{-3}$ in the 5 litre reactor.

Then, it is deduced the $N_2(X, v > 13)$ density by considering that the $N_2(B, v = 11)$ state in the pink afterglow is produced by the following dominant reaction:

$$N_2(A) + N_2(X, v > 13) \rightarrow N_2(B, v = 11) + N_2(X) \quad (c)$$

Then the ratio of $a_{N+N}\, I^m_{580}$ (late) and $(1 - a_{N+N})\, I^m_{580}$ (pink) afterglow is as follows:

$$\left(\frac{a_{N+N}}{1 - a_{N+N}}\right)[A][X, v > 13]k_e = [N]^2 k_a [N_2] \qquad (5)$$

From a_{N+N} values, N-atoms and $N_2(A)$ densities, it was determined the $N_2(X, v > 13)$ density. It is found a $N_2(X, v > 13)$ density of about $1\ 10^{13} cm^{-3}$ for N_2 and $Ar - 2\%N_2$, lower than the $5\ 10^{13} cm^{-3}$ value obtained in $Ar - 20\%N_2$.

5. Conclusions

By assuming a plateau [9] of $N_2(X, v > 5)$ density in the plasma up to $N_2(X, v = 13)$, it can be estimated a decrease of the $N_2(X, v > 13)$ density by about 10^3 between the plasma and the reactor entrance at a time of $3\ 10^{-3} s$ (plasma parameters 4 Torr, 1 slpm, 100 Watt, discharge tube dia.5 mm). Compared with the N-atom density, the $N_2(X, v > 13)$ density is one order of magnitude lower and with an energy of more than 3.5 eV, these vibrationnally excited molecules could act in addition to N-atoms in surface reactions.

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