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SPECTROSCOPY OF Ar-N₂ MICROWAVE FLOWING POST-DISCHARGES

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Résumé - La post-luminescence des décharges HF (13.6, 49.5 et 2450MHz) dans les mélanges Ar-N₂ à 100 Torr a été étudiée par spectroscopie d'émission. Les processus de recombinaison N + N + M₂ et N + C + M₂ (M₂ = Ar-N₂) ont été caractérisés. La densité des atomes de carbone dans la post-décharge a été déduite de la mesure des atomes d'azote par titration avec NO. Des rapports de densités C/M₂ aussi bas que 10⁻⁷ - 10⁻⁸ ont été trouvés dans des post-décharges à 100-200 Torr, avec des pourcentages élevés (33-100%) de N₂ dans Ar.

Abstract - The flowing afterglow of 100 Torr Ar-N₂ HF (13.6, 49.6 and 2450MHz) discharges has been studied by emission spectroscopy. The N + N + M₂ and N + C + M₂ (M₂=Ar-N₂) recombination processes have been characterized. From N density measurements by NO titration, it has been deduced the C density in the post-discharges. C/M₂ density ratios as low as 10⁻⁷-10⁻⁸ have been found in 100-200 Torr post-discharges with high percentages (33-100%) of N₂ in Ar.

1 - INTRODUCTION

A growing interest of nitrogen flowing post-discharges recently appeared in the file of surface coating processes. For steel surface nitriding, thick coatings of Fe₄N (5-8 μm of thickness) have been obtained from DC(1) and microwave (2) N₂ post-discharges.

In N₂ flowing post-discharges, the N atoms are producing the Lewis-Rayleigh afterglow by the following three body reaction:

where k_1 is the recombination rate and M₂ = Ar - xN₂ gas mixture.

It is the purpose of the present paper to study radiative emission in flowing afterglows of 100 Torr Ar-N₂ HF post-discharges. Such a gas pressure has been chosen to keep a constant power of about 100 Watts in the plasma when x is varying from 4 to 100%. Higher Ar-N₂ gas pressure plasmas, up to the atmospheric pressure, have been performed with such a low 100 Watts power but for x less than 10% in 2.45 GHz microwave discharges (3).

2 - THE EXPERIMENTAL SET UP

The experimental set up is reproduced in Fig.1.

Fig.1 - the Ar-N₂ microwave discharge and post-discharge set-up.

A surfatron (4) or a Ro-box (5) exciter is used to sustain an Ar-N₂ discharge in a 4mm Id, 6mm Od and 10cm long quartz tube. The two exciters have worked in the present experiment with HF frequencies of 910MHz, 2450MHz for the surfatron and 49.5MHz, 13.6 MHz for the Ro-box, respectively.

The flowing microwave discharge is related to a 10mm Id, 12mm Od, 10cm long post-discharge quartz tube via a side-armed tube to separate the discharge and post-discharge glows. The post-discharge tube is connected to a forepump to maintain a mean gas pressure between 10 and 300 Torr and flow rates from 0.25 to 10 Nlmin⁻¹.

The visible plasma glow in the discharge tube is extending axially over a few centimeters for a microwave power of about 100 Watts, depending on gas pressure and flow rate. Downstream the discharge an homogeneous afterglow is extending along the z-axis (cf. Fig.1) in the post-discharge tube which is an electric field free region. Upstream the post discharge, an Ar-1.3% NO gas mixture was introduced through a lateral gas inlet to determine the N atom densities by NO titration (3).

The optical emission lines are detected perpendicularly to the axis of the post-discharge tube by means of a quartz optical fiber which is connected to a spectrometer, using an Optical Spectrometric Multichannel Analyser (OSMA) for the photon spectrum analysis.

3 - RADIATIVE EMISSION IN THE Ar - N₂ FLOWING AFTERGLOW

The 1st pos. emission following the N-atom recombination (reaction i) has been detected along the axis of the post-discharge tube (cf. Fig.1). Spectrum of $\Delta V = 4$ sequence is reproduced in Fig.2 for Ar-4% N₂ gas mixture at 90 Torr, 100 Watts, Z = 9cm in the post-discharge.

Fig. 2 - Spectrum of N₂ 1st pos. in Ar-4% N₂ post-discharge at Z=9cm. $\Delta v = 4$ band sequence from $\lambda = 575.5\text{nm}$. (12-8) to $\lambda = 607\text{ nm}$. (6-2) with a resolution limit $\delta\lambda = 0.1\text{nm}$. Discharge surfatron 910 MHz, p = 90 Torr, 100 W, Q = 3 N ℓ min⁻¹.

The rotational structure of each vibrational band is obtained with a resolution limit of 4 Å. The corresponding rotational temperature is estimated to be 400(±50) K, keeping a nearly constant value for Ar-xN₂ mixtures with x = 4-100% at 100 Torr and 100 watts (6).

It has been observed a maximum in intensity of vibrational transitions coming from N₂(B,V'=11) levels for pure N₂ discharges. This maximum is scattered on lower levels N₂(B,V' = 11→7) in Ar - xN₂ with x < 10%, as shown in Fig.2. Such a result has been previously analysed (6) as coming from recombination process i) which mainly produced N₂(B,V' = 11) with M₂=N₂. In Ar-xN₂ gas mixture, the N₂(B,V'=11) peak is progressively decreasing in front of the N₂(B,V'=8) peak which is dominant for Ar-4% N₂.

By recording the blue-violet part of the post-discharge spectrum, it has been

observed a strong emission of CN radical as reproduced in Fig.3, for a N_2 100 Torr, 100 Watts, 49.5 MHz post-discharge.

Fig.3 - Spectrum of CN violet system in N_2 post-discharge at $Z = 7$ cm. $\Delta v = 0$ band at $\lambda = 388.3$ nm (0,0) and $\lambda = 384.7$ nm (7,7) with a resolution limit $\delta\lambda = 0.1$ nm. Discharge Ro-box 49.5 MHz, $p = 100$ Torr, 160 W, $Q = 2$ Nl min $^{-1}$.

The CN-emission comes from $CN(B^2\Sigma^+, V')$ excited levels. It appears in Fig.3 a strong emission from $CN(B, V'=7)$ near the well known emission from $CN(B, V'=0)$. The band emission from $CN(B, V'=7)$ is produced by recombination of N and C atoms, following the three body reaction:

with $k_2 = 9.4 (\pm 2.5) \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$ for $M_2 = \text{Ar-N}_2$ as established in ref.7. Kinetics of $N_2(B, V')$ and $CN(B, 7)$ excited states produced in the afterglow by the recombination processes i) and ii) is now analysed.

4 - INTENSITIES OF $N_2(B, V')$ AND $CN(B, 7)$ RADIATIVE STATES IN THE FLOWING AFTERGLOW: DETERMINATION OF CARBON ATOM DENSITIES

The $N_2(B, V')$ states are produced by reaction i) in post-discharge regime and destroyed by photon emission of frequency $\nu_1^r(V')$ and by the following quenching reaction:

Then the density of $N_2(B, V')$ can be written as:

$$[N_2(B, V')] = [N]^2 \frac{[M_2] k_1(V')}{\nu_1^r(V') + [M_2] k_3(V')} \quad (1)$$

where the data on $k_1(V')$ and $k_3(V')$ rate coefficients and $\nu_1^r(V')$ frequency are reproduced in ref.6.

As for the $CN(B, 7)$ state, it is produced by reaction ii) and destroyed by radiative emission of frequency $\nu_2^r(7)$ and by the following quenching reaction:

It follows the $CN(B, 7)$ density as:

$$[CN(B, 7)] = \frac{[C] [N] [M_2] k_2(7)}{\nu_2^r(7) + [M_2] k_4(7)} \quad (2)$$

The radiative frequencies and quenching rates of $CN(B, 7)$ are given in ref.7 and 8, respectively.

The vibrational band intensity $I(V', V'')$ is related to the radiative state density $[R(V')]$ by the following equation:

$$I(V', V'') = \frac{C(\lambda)}{\lambda} [R(V')] \nu^r(V', V'') \quad (3)$$

where λ is the emitted wavelength, $C(\lambda)$ is a factor related to spectral response of the detection system and $\nu^r(V', V'')$ is the transition probability.

From eq.(1-3) the intensity ratio of $CN(B, 7 - X, 7)$: $I_2(7, 7)$ and $N_2(B, V' - A, V'')$: $I_1(V', V'')$ is given by:

$$\frac{I_2(7, 7)}{I_1(V', V'')} = \frac{C_2(7, 7)/\lambda_2(7, 7)}{C_1(V', V'')/\lambda_1(V', V'')} \frac{[C]}{[N]} \frac{k_2(7)}{k_1(V')} \frac{Q_1(V', V'')}{Q_2(7, 7)} \quad (4)$$

$$\text{with } Q_1(V', V'') = \frac{\nu_1^r(V')}{\nu_1^r(V', V'')} \left(1 + \frac{[M_2] k_3[V']}{\nu_1^r[V']} \right)$$

$$\text{and } Q_2(7, 7) = \frac{\nu_2^r(7)}{\nu_2^r(7, 7)} \left(1 + \frac{[M_2] k_4(7)}{\nu_2^r(7)} \right).$$

By considering eq.4, it can be deduced the carbon atom densities from measurements of $I_2(7, 7)/I_1(V', V'')$ and $[N]$, respectively. The N-atom densities have been

determined by NO titration with the experimental set up of Fig. 1 (3,6). After calibration the spectra response of the optical spectrometer in Fig.1 and by considering the $\lambda_1(9,5)$ band head in Ar-N₂ gas mixtures, it has been found that:

$$\frac{C_2(7,7)/\lambda_2(7,7)}{C_1(9,5)/\lambda_1(9,4)} \sim 1 \text{ in eq. 4.}$$

The $Q_1(9,5)$ and $Q_2(7,7)$ terms in eq.4 are simplified with $\nu_1^r(9) \sim \nu_1^r(9,5) = 6.7 \times 10^4 \text{ s}^{-1}$ [9] and $\nu_2^r(7) \sim \nu_2^r(7,7) = 2.5 \times 10^7 \text{ s}^{-1}$ (7).

As the $k_4(7)$ rate coefficient is largely less than $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (8), it can be deduced in Ar-N₂ at $p \sim 100$ Torr that $[M_2]k_4(7)$ is less than $\nu_2^r(7)$ so that $Q_2(7,7) \sim 1$. Inversely $[M_2]k_3(9)$ is larger than $\nu_1^r(9)$ and eq.4 becomes:

$$\frac{I_2(7,7)}{I_1(9,5)} = \frac{[C]}{[N]} \frac{k_2(7)}{k_1(9)} \frac{[M_2]k_3(9)}{\nu_1^r(9)} \quad (5)$$

In Ar-33% N₂ gas mixture at $p=100$ Torr ($M_2 = 3 \times 10^{18} \text{ cm}^{-3}$), $k_2(7)=10^{-32} \text{ cm}^6 \text{ s}^{-1}$ (7), $k_1(9) = 2.6 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$ and $k_3(9) = 2.35 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (cf. ref. 6).

Then it can be calculated:

$$\frac{I_2(7,7)}{I_1(9,5)} = 4 \times 10^4 \frac{[C]}{[N]} \quad (6)$$

It has been measured $[N] = 5(\pm 1.5) \times 10^{15} \text{ cm}^{-3}$ by NO titration and $\frac{I_2(7,7)}{I_1(9,5)} \sim 0.4$ in

Ar-33% N₂ gas mixture. It results: $[C] \sim 5 \times 10^{10} \text{ cm}^{-3}$.

This method has given C-atom densities between 2×10^{10} and $4 \times 10^{11} \text{ cm}^{-3}$ in the afterglow for high percentages of N₂ in Argon (33,50 and 100%), at pressures of 100 and 200 Torr. The HF plasmas were initiated by Ro-box (13.6 and 49.5MHz) and surfatron (2.45GHz) exciters (cf. Fig.1).

5 - CONCLUDING REMARKS

From the spectroscopic analysis of Ar-N₂ afterglows produced by HF discharges, the two recombination processes: $N+N+M_2$ and $C+N+M_2$, with $M_2 = \text{Ar-N}_2$ as a third body, have been characterized. The N atom densities have been measured by NO titration and from the studied N and C-atom kinetics in the post-discharge, it has been deduced the C-atom densities. This method is very sensitive for impurity detection in high pressure (100-200 Torr) $M_2 = \text{Ar-N}_2$ post-discharges, since C/ M_2 ratios of 10^{-7} - 10^{-8} have been measured.

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