Densities of N and H atoms in $R/x\%(N_2-5\%H_2)$ (R = Ar or He) microwave flowing afterglows

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Abstract: Afterglows of $R/x(N_2-5\%H_2)$ (R=Ar or He) flowing microwave discharges are characterized by optical emission spectroscopy. Absolute densities of N atoms and $N_2(A)$ and $N_2(X,v>13)$ molecules and estimated densities of NH and H atoms are determined after calibration of the N atom density by NO titration. Conditions allowing to obtain high N and H atoms densities in the early afterglow region of $R/x(N_2-5\%H_2)$ mixtures with x<5% are given.

Keywords: Afterglows, N and H atoms, Optical Emission Spectroscopy.

1. Introduction

Afterglows of N₂ flowing microwave discharges have previously been studied at medium gas pressures (1-20 Torr) for the sterilization of medical instruments by Natoms^{1,2}. Recently^{3,4}, it has been observed an enhanced nitriding of TiO₂ films in the flowing afterglow of N₂/2%H₂ microwave and RF plasmas, which was attributed to the presence of H and N atoms.

In the present study, flowing afterglows produced by $R/x\%(N_2-5\%H_2)$ (R = Ar or He) microwave plasmas have been studied by emission spectroscopy. Intensities emitted by the 11-7 band of the N₂ first positive system (1+) at 580 nm (I₅₈₀) and by the 1-0 band of the N₂ second positive system (2+) at 316 nm (I₃₁₆) were measured to obtain the absolute concentrations of N-atoms, N₂(A) and N₂(X,v>13) after NO titration to calibrate the N-atom density. Moreover, the NH and H-atom densities were estimated by choosing the appropriated kinetic reactions at the origin of the NH 336 nm emission.

2. Experimental set-up

The used experimental setup is reported in Fig. 1.^{1-2,5}. Ar/N₂ and He/N₂ microwave discharges were produced by a surfatron cavity operating at 2.45 GHz. In these mixtures, the plasma length was found to extend between 2 to 20 cm after the surfatron gap, depending on the N₂ amount and on the HF power. With a discharge tube of 5 mm i.d. and 20 cm in length, connected to a bent postdischarge tube of 18 mm i.d. and 50cm in length, the residence time of the afterglow at z = 3 cm after the beginning of the 18 mm post-discharge tube is 10^{-3} s.

A pre-mixed N_2 -5% H_2 gas can be introduced instead of N_2 to produce NH radicals and H-atoms in addition to the N_2 active species.

In previous works^{6,7}, first results were presented for the same $R/x(N_2-5\%H_2)$ (R=Ar or He) gas mixtures with $x \ge 20\%$. The present paper focuses on early afterglow conditions (z = 3 cm) and low N₂-5%H₂ percentages (x = 2-10%).

Constant operating conditions were used, with a total gas flow rate $Q_{total} = 1.0$ slpm, a pressure of 8 Torr and an

injected microwave power $P_{MW} = 150$ W, that previously allow obtaining high concentrations of active species in the late afterglows of N₂/He and N₂/H₂ mixtures^{6,7}.

 TiO_2 samples can eventually be exposed (heated or not) in a 5 litres Pyrex reactor following the afterglow tube (results not shown in this paper).

Optical Emission Spectroscopy (OES) along the afterglow tubes was performed using an optical fibre connected to an Acton Spectra Pro 2500i spectrometer (grating 600 gr/mm), equipped with a Pixis 256E CCD detector (front illuminated 1024x 256 pixels).



Fig. 1. Photo and scheme of the microwave flowing afterglow experimental setup.

3. Active species densities in $R/2-10\%(N_2-5\%H_2)$ afterglows (R = Ar or He)

3.1. N-atom, N₂(A) and N₂(X, v>13) densities

In flowing afterglows, absolute N atom densities can be obtained by NO titration. In full late afterglow conditions, the N₂ (1+) (11-7) band emission at 580 nm (I₅₈₀) is produced by the 3-body recombination process of N atoms:

$$N(^{4}S) + N(^{4}S) + M \rightarrow N_{2}(B,v'=11) + M$$
 (a)

$$N_2(B,v=11) \rightarrow N_2(A,v=7) + hv (1+, 580nm)$$
 (a')

In the early afterglow, here defined as the afterglow region lying between the pink and the late afterglow, only a fraction (a_{N+N} , with 0< a_{N+N} <1) of the I₅₈₀ emission is due to the process (a), the remaining fraction being caused by collisions between high vibrationally excited levels of the ground molecular state N₂(X,v>13) and metastable states N₂(A):

$$N_2(X,v>13) + N_2(A) \rightarrow N_2(B,0\le v''<12) + N_2(X,w)$$
 (b)

In consequence, in the early afterglow region, the N atom concentration can be related to the a_{N+N} fraction of the observed I_{580} emission through the proportionality relation (possible quenching by H_2 molecules was neglected):

$$a_{N+N}I_{580} = k_1[N]^2 \tag{1}$$

 k_1

$$= c_{580} \frac{hc}{580} A_{A,7}^{B,11} \frac{k_a}{\left(v_{N_2(B,11)}^R + [R]k_{N_2(B,11)}^{Q_R} + [N_2]k_{N_2(B,11)}^{Q_{N_2}}\right)}$$

where c_{580} is the spectral response of the intensity acquisition system at 580 nm, $A_{A,7}^{B,11}$ is the vibrational transition probability (7.8 10⁴ s⁻¹) of the (1+, 11-7) band, k_a is the rate coefficient for reaction (a), varying from k_a = 9 10⁻³⁴ cm⁶s⁻¹ in pure N₂ and in Ar/50%N₂ to 3 10⁻³⁴ cm⁶s⁻¹ in Ar/2%N₂ and $k_a = 4 10^{-34}$ cm⁶s⁻¹ in He/(5-40%)N₂, $v_{N_2(B,11)}^R$ and $k_{N_2(B,11)}^{Q_i}$ are respectively the radiative loss frequency and the quenching rates of the N₂(B,11) level by species i ($v_{N_2(B,11)}^R = 2 10^5$ s⁻¹, $k_{N_2(B,11)}^{Q_{N_2}} = 3 10^{-11}$ cm³s⁻¹, $k_{N_2(B,11)}^{Q_{Ar}} = 0.2 10^{-11}$ cm³s⁻¹ and $k_{N_2(B,11)}^{Q_{H_2}} = 10^{-12}$ cm³s⁻¹).

As reported by Ricard et al.^{7,8}, the $N_2(A)$ and $N_2(X,v>13)$ densities can be deduced from the N-atom density by line ratio methods. Assuming reaction (c) is the dominant process for the production of the $N_2(C,v'=1)$ level:

$$N_2(A) + N_2(A) \rightarrow N_2(C, v'=1) + N_2(X)$$
 (c)

$$N_2(C,v'=1) \rightarrow N_2(B,v''=0) + hv (2+, 316nm)$$
 (c')

$$I_{316} = k_2 [N_2(A)]^2$$
 (2)

 k_2

$$= c_{316} \frac{hc}{316} A_{B,0}^{C,1} \frac{k_c}{\left(v_{N_2(C,1)}^R + [R]k_{N_2(C,1)}^{Q_R} + [N_2]k_{N_2(C,1)}^{Q_{N_2}}\right)}$$

Using the same definitions than above and with $A_{B,0}^{C,1} = 1.3 \ 10^7 \ s^{-1}$, $k_c = 4 \ 10^{-11} \ cm^3 s^{-1}$, $v_{N_2(C,1)}^R = 2.7 \ 10^7 \ s^{-1}$, $k_{N_2(C,1)}^{Q_{N_2}} = 3 \ 10^{-11} \ cm^3 s^{-1}$, $k_{N_2(C,1)}^{Q_{AT}} = 5 \ 10^{-12} \ cm^3 s^{-1}$ and $k_{N_2(C,1)}^{Q_{H_2}} = 2 \ 10^{-12} \ cm^3 s^{-1}$, it comes:

$$a_{N+N} \frac{I_{580}}{I_{316}} = k_3 \left(\frac{[N]}{[N_2(A)]}\right)^2 \tag{3}$$

where $k_3 = \frac{k_1}{k_2} = 2.5(\pm 0.5) \ 10^{-7}$ in Ar/>10% N₂ and He/>10% N₂ and $k_3 = 4 \ 10^{-7}$ in Ar/(2-5%)N₂, with $\frac{c_{580}}{c_{316}} = 7$.

Assuming now that in the early afterglow, $N_2(B,v=11)$ levels can also be produced by reactions (b), it follows:

$$\frac{a_{N+N}}{1-a_{N+N}} = k_4 \frac{[N]^2}{([N_2(A)][N_2(X,\nu>13)])}$$
(4)

where it is calculated $k_4 = \frac{k_1}{k_b} = 7 \ 10^{-6}$ in Ar/>2% N₂ and in He/>80% N₂, slowly decreasing to $k_4 = 5 \ 10^{-6}$ in He/(60-80%) N₂, $k_4 = 3 \ 10^{-6}$ in He/(10-40%) N₂ and $k_4 = 2 \ 10^{-6}$ in He/(2-5%) N₂.

The estimated uncertainties in the determination of species densities are 30% for N-atoms, 60% for N₂(A) and only the order of magnitude for N₂(X,v>13), mainly depending on the uncertainty in the determination of the $\frac{a_{N+N}}{1-a_{N+N}}$ coefficient.

3.2. NH radical and H-atom densities

As previously reported⁷, it is estimated that the reaction (d) is the most efficient source of NH(A) excitation:

$$N_2(X,v>13) + NH \rightarrow N_2 + NH(A,v=0)$$
 (d)
NH(A,v=0) \rightarrow NH(X,v=0) + hv (336 nm) (e)

The same intensity ratio method that the one developed in Section 3.1. can be applied to determine the absolute NH radical density, conducing to:

$$I_{336} = k_5[NH][N_2(X, v > 13)]$$
(5)

$$k_5$$

$$= c_{336} \frac{hc}{336} A_{X,0}^{A,0} \frac{k_d}{\left(v_{NH(A,0)}^R + [R]k_{NH(A,0)}^{Q_R} + [N_2]k_{NH(A,0)}^{Q_{N_2}}\right)}$$

$$a_{N+N} \frac{I_{580}}{I_{336}} = k_6 \frac{[N]^2}{([NH][N_2(X,\nu>13)])}$$
(6)

With $\frac{c_{580}}{c_{336}} = 5$ and $A_{X,0}^{A,0} = v_{NH(A,0)}^R = 2 \ 10^6 \ s^{-1}$, $k_d = 5 \ 10^{-11} \ cm^3 s^{-1}$ (chosen to be equal to the rates of the N₂(X,v>13) + N₂(A) \rightarrow N₂ + N₂(B,11) and N₂(X,v>13) + N₂⁺ \rightarrow N₂ + N₂⁺(B) exothermic reactions),

 $k_{NH(A,0)}^{Q_{N_2}}$, $k_{NH(A,0)}^{Q_{Ar}}$ and $k_{NH(A,0)}^{Q_{He}} < 9 \ 10^{-14} \ \text{cm}^3 \text{s}^{-1}$ and $k_{NH(A,0)}^{Q_{H_2}} = 5 \ 10^{-11} \ \text{cm}^3 \text{s}^{-1}$, it is calculated $k_6 = \frac{k_1}{k_5} = 1.3 \ 10^{-7}$ in pure N₂ and in Ar/>40%N₂, $k_6 = 3.0 \ 10^{-7}$ in Ar/<40%N₂ and $k_6 = 2.0 \ (\pm 0.5) \ 10^{-7}$ in He/>2%N₂.

The H-atom and NH radical densities are related by the following kinetics:

$$N + H + M \rightarrow NH + M \tag{f}$$

$$N + NH \rightarrow H + N_2$$
 (g)

where the $k_f = 5(\pm 3) \ 10^{-32} \ cm^6 s^{-1}$ and $k_g = 5 \ 10^{-11} \ cm^3 s^{-1}$ rate coefficients are respectively given by Brown⁹ and Tatarova¹⁰.

Using the pseudo-stationary approximation and considering the k_f rate coefficient independent of the third body $(k_f^{N_2} = k_f^{Ar} = k_f^{He})$, it comes at 8 Torr:



Fig. 2a Spectrum measured in the $Ar/2\%(N_2-5\%H_2)$ afterglow at z = 3 cm (8 Torr, 1 slpm, 150 W, 0.4 ms) between 300 and 400 nm.



Fig. 2b $\Delta v = -4$ sequence of the N₂ 1+ spectrum measured in the Ar/2%(N₂-5%H₂) afterglow at z = 3 cm (8 Torr, 1 slpm, 150 W, 0.4 ms.

Fig. 2 reproduces spectra measured at z = 3 cm in the Ar/2%(N₂-5%H₂) mixture at 8 Torr, 1 slpm and 150W. In the 300-400 nm spectral range, the NH (0-0) and (1-1) bands at respectively 336 and 337 nm are the most intense emissions. It is also observed the N₂ 2+ (1-0) band at 316 nm, the NO β (0-8) band at 320 nm and the N₂⁺ (0-0) band at 391 nm, close to the CN violet bands between 385 and 388 nm. For data treatment, the NH (1-1) band at 337 has been discarded because of possible mixing with the N₂ 2+ (0-0) band at 337 nm. The I₃₃₆ intensity is thus measured from the half intensity of the I₃₃₆ and I₃₃₇ band junction.

The N₂ 1+ spectrum emitted by the $\Delta v = -4$ sequence is reproduced in Fig. 2b, for the same experimental conditions.

As shown by Ricard⁷, by considering the I_{11}/I_9 ratio, the a_{N+N} coefficient can be deduced from the vibrational distribution observed in Fig. 2b. With the experimental conditions of Fig. 2, it is found the value $a_{N+N} = 0.35$ and after calibration by NO titration, it is deduced [N] = 1.0 10^{15} cm⁻³.

In previous studies⁷, the NH and H densities were obtained in $N_2/2.5\%H_2$, $Ar/50\%(N_2-5\%H_2)$ and $He/80\%(N_2-5\%H_2)$ gas mixtures. For $N_2/2.5\%H_2$ and $Ar/50\%(N_2-5\%H_2)$, it was found a [H]/2[H₂] dissociation rates of about 0.3%. In the $He/80\%(N_2-5\%H_2)$ mixture, the hydrogen dissociation rate was found to be higher (1.0%) and it was obtained a [H]/[N] ratio of about 30%.

According to eq. (6), the accuracy of the determination of the [NH] density largely depends on the accuracy of the [N₂(X,v>13)] density (limited to the order of magnitude) and on the choice of the k_d rate coefficient for reaction (d), chosen to be similar to the one of the N₂(X,v>13) + N₂(A) \rightarrow N₂ + N₂(B,11) and N₂(X,v>13) + N₂⁺ \rightarrow N₂ + N₂⁺(B) exothermic reactions⁷ (k_e = 5 10⁻¹¹ cm³s⁻¹).

As the H density is related to the NH density through eq (7) and to the k_f rate coefficient of 5 10^{-32} cm⁶s⁻¹ of the 3body recombination N + H + M \rightarrow NH + M, it is clear that the presented absolute densities of NH radicals and H atoms are highly speculative. Nevertheless, their relative variations with R(He or Ar) and with the dilution x of the (N₂-5%H₂) mixture in the rare gas remain significant.

Table 1 compares the a_{N+N} coefficients and the absolute densities obtained at z = 3 cm using the line ratio methods in the He/x(N₂-5%H₂) and the Ar/x(N₂-5%H₂), for x varying between 2 and 10% (8 Torr, 1slpm, 150 Watt).

With He and for x<20%, the accuracy of the abacus given in Fig. 3a and showing the variation of the I_{11}/I_9 ratio is too low and it has been chosen to use instead the I_{11}/I_9 ratio, given in Fig. 3b.

At low dilutions (2% and 5%), N-atom, $N_2(A)$ and $N_2(X,v>13)$ densities are higher in $Ar/x(N_2-5\%H_2)$ mixtures than in He/x(N₂-5%H₂), which is not the case at higher dilutions (10%).

Table 1. a_{N+N} coefficients, active species densities and dissociation rates determined at z = 3 cm in the early afterglows of R/x%(N₂-5%H₂) gas mixtures with R=He or Ar and x=2-10% (8 Torr, 1 slpm and 150 W). The [NH] and [H] densities are calculated with N₂(X,v>13) + NH and N + H + M rate coefficients of 5 10^{-11} cm³s⁻¹ and 5 10^{-32} cm⁶s⁻¹.* a_{N+N} calculated from

I ₁₁ /I ₁₀ . (8 Torr, 1slpm, 150 Watt)			
$R/x(N_2-5\%H_2)$	2%	5%	10%
a _{N+N}	$\begin{array}{ll} R = He & 0.6* \\ R = Ar & 0.35 \end{array}$	$\begin{array}{ll} R = He & 0.3* \\ R = Ar & 0.6 \end{array}$	$R = He \ 1.0-0.3*$ $R = Ar \ 0.7$
[N] (10 ¹⁵ cm ⁻³)	$\begin{array}{ll} R = He & 0.8* \\ R = Ar & 1.0 \end{array}$	$\begin{array}{ll} R = He & 0.7* \\ R = Ar & 2.2 \end{array}$	R = He 1.5-1.2* R = Ar 1.1
$[N_2(A)]$ (10 ¹¹ cm ⁻³)	$\begin{array}{ll} R = He & 2.3* \\ R = Ar & 4.0 \end{array}$	$\begin{array}{ll} R = He & 2.5* \\ R = Ar & 3.5 \end{array}$	$\begin{array}{ll} R = He & 2 \cdot 3^* \\ R = Ar & 1.0 \end{array}$
$[N_2(X,v>13)]$ (10 ¹³ cm ⁻³)	$\begin{array}{ll} R = He & 0.5* \\ R = Ar & 3.0 \end{array}$	$ \begin{array}{ll} R = He & 1.4* \\ R = Ar & 6.4 \end{array} $	$\begin{array}{ll} R = He & 3.5* \\ R = Ar & 3.6 \end{array}$
[NH] $(10^{10} \text{ cm}^{-3})$	$\begin{array}{ll} R = He & 7* \\ R = Ar & 2 \end{array}$	$\begin{array}{ll} R = He & 3^* \\ R = Ar & 0.1 \end{array}$	$ \begin{array}{ll} R = He & 0.3* \\ R = Ar & 0.04 \end{array} $
[H] $(10^{14} \text{ cm}^{-3})$	$\begin{array}{ll} R = He & 0.3* \\ R = Ar & 0.8 \end{array}$	$\begin{array}{ll} R = He & 0.1* \\ R = Ar & 0.05 \end{array}$	$ \begin{array}{ll} R = He & 0.1* \\ R = Ar & 0.02 \end{array} $
[H]/2[H ₂] (%)	$\begin{array}{c} R = He & 6^* \\ R = Ar & 15 \end{array}$	$\begin{array}{ll} R = He & 0.8* \\ R = Ar & 0.4 \end{array}$	$\begin{array}{ll} R = He & 0.4* \\ R = Ar & 0.08 \end{array}$
[N]/2[N ₂] (%)	$\begin{array}{ll} R = He & 8^* \\ R = Ar & 10 \end{array}$	$\begin{array}{ll} R = He & 3^* \\ R = Ar & 9 \end{array}$	$\begin{array}{ll} R = He & 2* \\ R = Ar & 2 \end{array}$



Fig. 3 Variation of the I_{11}/I_9 (3a) and I_{11}/I_{10} (3b) band intensity ratios in the mixed region between the pink afterglow ($a_{N+N} = 0$) and the full late afterglow ($a_{N+N} = 1$) for the He/x(N₂-5%H₂) mixtures.

The NH concentration decreases with x in both mixtures and is higher in He mixtures than in Ar mixtures. In both mixtures the H-atom concentration and the hydrogen dissociation rate strongly increase for x < 5%, with values of about 15% with R = Ar and 6% with R = He.

In comparison, the nitrogen dissociation rate, which is usually less than 1% in pure N₂ afterglows,¹¹ increases by one order of magnitude with high dilution in Ar, to reach 10% in the $Ar/2\%(N_2-5\%H_2)$ mixture.

4. Conclusions

Early afterglows of $R/x\%(N_2-5\%H_2)$ (R = Ar or He) gas mixtures have been studied to obtain the absolute densities of N-atoms, $N_2(A)$ and $N_2(X,v>13)$ metastable molecules by line intensity ratio methods, after calibration of the N-atom density by NO titration. The line intensity ratio method also allowed estimating the density of NH radicals and H-atoms.

For this evaluation, a rate coefficient of 5 10^{-11} cm³s⁻¹ has been considered for the reaction N₂(X,v>13) + NH \rightarrow N₂ + NH(A,v=0) and a rate coefficient of 5 10^{-32} cm⁶s⁻¹ for the N + H + M \rightarrow NH + M 3-body recombination.

Such values conduce to high dissociation rates of H_2 and N_2 in $R/x\%(N_2-5\%H_2)$ early afterglows with R = Aror He and x<5% at 8 Torr, 1 slpm, 150 Watt.

Appearing to be a rich source of NH radicals and H atoms, accompanying dominant N-atoms, the $R/N_2/H_2$ (R = Ar or He) afterglows are of interest for surface treatments, as already observed for selective surface nitridation of TiO₂ films^{3,4}.

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