Active species densities in R/x%N₂ and R/x%(N₂-5%H₂) (R = Ar or He) microwave early afterglows

A. Ricard and J.P. Sarrette

LAPLACE, Université de Toulouse, CNRS, INPT, UPS 118 route Narbonne, 31062 Toulouse Cedex 9, France

E-mail : ricard@laplace.univ-tlse.fr

Key words Afterglows, N and H-atoms, N₂ metastable molecules, NH radicals, N₂⁺ ions

Abstract

Afterglows of R/x%N₂ and R/x%(N₂-5%H₂) (R = Ar or He) flowing microwave discharges are characterized by optical emission spectroscopy. Absolute densities of N-atoms, N₂(A) and N₂(X,v>13) metastable molecules and N₂⁺ ions and evaluated densities of NH and H are determined after calibration of the N—atom density by NO titration. New results on NH radical and H-atom relative densities are obtained by considering that the excitation of the NH(A) radiative state in the afterglow is produced by N₂(X,v>13) + NH collisions. The interest of these results concerns the enhancement of surface nitriding by combined effects of N and H atoms inclusion in afterglow conditions.

1. Introduction

Afterglows of N₂ flowing microwave discharges have previously been studied at medium gas pressures (1-20 Torr) for the metal surface nitriding [1,2], carbo-nitriding [3] and plasma cleaning sterilization of medical instruments by N-atoms [4,5,6]. The addition of a small percentage of H₂ into N₂ has previously investigated and a slight maximum of the N-atom density was observed with the N₂/0.4%H₂ gas mixture, correlated to a paper wettability increase [7].

Recently [8], it has been observed an enhanced nitriding of TiO₂ films in the afterglow of N₂/2%H₂ microwave plasmas which was attributed to the presence of H with N atoms. In the present study, early flowing afterglows produced by R/x%N₂ and R/x%(N₂-5%H₂) (R = Ar or He) microwave plasmas are studied by emission spectroscopy up to high N₂ dilutions (95%), with the same experimental arrangement than used in [7,9]. The interest of the N₂ dilution into Ar and He is to increase the electron energy in the plasma by minoring the effect of the electron vibrational barriers at 3 eV in pure N₂.

The electron energy should also be higher in He containing plasmas as a result of lower electron excitation cross section (~ 3 x 10⁻¹⁸ cm²), compared to Ar (~ 3 x 10⁻¹⁷ cm²) and N₂ (~ 3 x 10⁻¹⁶ cm²) and higher excitation threshold (19 eV in He and 12 eV in Ar) [10]. In addition, a special effect in Ar plasma is the Ramsauer minimum about 0.3 eV with the consequence to increase the electron density and to produce long plasma column [9b].

Changes of the electron energy and density in the plasma, induced by N₂ dilution into Ar and He, are presently studied through the active species production in two regions of the afterglow:

- the early afterglow region at times of 10⁻³ s where the pink afterglow emission is dominant;
- the mixed afterglow region at times of 3 x 10⁻² s where the late afterglow emission superimposes with the pink afterglow emission.
Intensities emitted by the N$_2$ first positive system (1+) at 580 nm (11-7 band), the N$_2$ second positive system (2+) at 316 nm (1-0 band) and the N$_2^+$ first negative system (1-) at 391 nm (0-0 band) were measured to obtain the N, N$_2$(A), N$_2$(X,v>13) and N$_2^+$ absolute densities after NO titration to calibrate the N-atom densities [9]. NH and H-atom densities are estimated by choosing the appropriated kinetic reaction scheme at the origin of the NH 336 nm emission.

2. Experimental setup

The used experimental setup is reported in previous publication [5-8,9]. It is reproduced in Fig.1.

![Fig.1 Microwave flowing afterglow set up. The microwave discharge is produced in a quartz tube of dia.5mm, length 20 cm enlarging in an afterglow bent tube of dia.18 mm, length 30 cm connected to a 5 litre Pyrex reactor.](image)

The discharge is located inside a 5 mm dia. quartz tube with a plasma length varying from 2 to 20 cm after the surfatron gap, depending on the N$_2$ amount in the gas mixtures and on the HF power. With a discharge tube length of 20 cm after the surfatron gap, the residence time of the afterglow in the dia.18 mm tube before the 5 litre reactor is 10$^{-3}$ s at z = 3 cm, 3 10$^{-2}$ s at z = 20 cm and 10$^{-1}$ s at z = 50 cm.

A pre-mixed N$_2$-5%H$_2$ gas can also be introduced instead of N$_2$ to produce NH radicals and H-atoms in addition to the N$_2$ active species.

The absolute N atom density was obtained from the I$_{580}$ measured intensity after calibration by NO titration. During calibration, an Ar-2%NO gas mixture was introduced in the 18 mm dia tube, as shown in Fig.1.

The R/x%N$_2$ and R/x%(N$_2$-5%H$_2$)(R=Ar or He) microwave plasmas are produced by a surfatron cavity at 2450 MHz, power 100-200 Watt, flow rate 0.5-2.0 slm and gas pressure between 2 and 8 Torr. It is presently reported results obtained at 8 Torr, 1 slm and 150 Watt.
The optical emission spectroscopy 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 slit aperture was fixed at 150 µm and the integration time at 1 s.

### 3. Plasma and early afterglow emissions in Ar/x%N₂ and He/x%N₂ gas mixtures at 8 Torr, 1 slm, 150 Watt.

To be certain that the detected afterglow intensity at z = 3 cm is not perturbed by the intense plasma light, it is pointed out the following characteristics of the plasma and afterglow emissions in the used conditions of 8 Torr, 1 slm and 150 Watt:

- The intensity ratio N₂ 2⁺ (316 nm)/N₂ 1⁺ (580 nm) varies between 3 and 10 inside the N₂ plasma where the collisions of electrons and metastable atoms are the dominant excitation process of the emitting states. The same intensity ratio is only 0.2 in the afterglow at z = 3 cm where the N⁺N recombination increases the N₂ 1⁺ (580 nm) intensity.
- As pointed out in [11], the N₂ 1⁺ (2-0) band shows a double head structure between 770 and 775 nm, that can be used to monitor the gas temperature. With this method, it was found a temperature of 700 K in the N₂ plasma, decreasing to 360 K in the early afterglow.
- The A+/A⁻ factor is 0 in the plasma (absence of A+/A⁻ recombination in front of the e + N₂ collisions to populate the N₂(B) states) and 0.2-0.3 in the N₂ early afterglow at z = 3 cm (20-30% of A+/A⁻ recombination).

The early afterglow intensity can therefore be separated from plasma intensity conditions at z = 3 cm when the following conditions are fulfilled:

\[ R = \frac{I_{316}}{I_{580}} < 1, \ T_{\text{gas}} = 300-400 \ K \] and \( a_{N+N} > 0 \).

At z = 20 cm, just after the shoulder in Fig. 1, the afterglow and plasma light are well separated with a homogenous radial distribution of the afterglow light. It is presently given first results at z = 20 cm in R/x%N₂, then at z = 3 cm in R/x%(N₂-5%H₂), where it is expected high H₂ dissociation.

### 4. Active species densities in Ar/x%N₂ and He/x%N₂ afterglows at z = 20 cm, 8 Torr, 1 slm, 150 Watt.

In [5], results were presented for Ar/N₂ mixtures at z = 3 cm in early afterglow conditions. Densities of N-atoms, N₂(A) and N₂(X,v>13) metastable molecules and N₂⁺ ions are presently determined at z = 20 cm in Ar/x%N₂ and He/x%N₂ afterglows. The position z = 20 cm (corresponding to an afterglow time of \( 3 \times 10^{-2} \) s) was chosen because at this point, the I₅₈₀ emission is closer to a late afterglow emission and the radial heterogeneity of the pink afterglow as demonstrated in [8] was avoided.

The N₂(580 nm) band head intensity (I₅₈₀) is related to the N-atom density as follows:

\[ I_{580} = k_1 [N]^2 \]  

with \( k_1 = \frac{c(580) (hc/580) A(580) k_3[M]}{[M] (v_{B,11}^B + [M] k_{B,11}^O)} \).

The \( k_3 \) rate coefficient corresponds to the 3-body recombination reaction:

\[ N + N + M \rightarrow N_2(B,v'=11) + M \]
where M is the Ar/x%N\textsubscript{2} or He/x%N\textsubscript{2} gas mixture.

In k\textsubscript{1}, c(580) is the spectral response of the monochromator modified by the transmission rate of light through the tube at 580 nm, \( \text{A}(580) \) is the N\textsubscript{2} 1\textsuperscript{+} (11-7) vibrational transition probability (7.8 \( \text{10}^{4} \ \text{s}^{-1} \)). The \( k_\text{s} \) rate coefficient varies as follows: \( k_\text{s} = 9 \ 10^{-34} \ \text{cm}^6\text{s}^{-1} \) in pure N\textsubscript{2} and in Ar/50\%N\textsubscript{2}, decreasing to \( 1 \ 10^{-34} \ \text{cm}^6\text{s}^{-1} \) in Ar/4\%N\textsubscript{2} [13] and \( k_\text{s} = 4 \ 10^{-34} \ \text{cm}^6\text{s}^{-1} \) in He/(5-40%)N\textsubscript{2} [14]. \( \nu^{\text{R},\text{B},11} \) and \( k^{\text{Q},\text{B},11} \) are respectively the radiative frequency and the quenching rate coefficient of the N\textsubscript{2}(B,11) state (\( \nu^{\text{R},\text{B},11} = 2 \ 10^{5} \ \text{s}^{-1} \), \( k^{\text{N},\text{B},11} = 3 \ 10^{11} \ \text{cm}^3\text{s}^{-1} \), \( k^{\text{He},\text{B},11} = 0.2 \ 10^{11} \ \text{cm}^3\text{s}^{-1} \) and \( k^{\text{He},\text{B},11} = 10^{12} \ \text{cm}^3\text{s}^{-1} \) [13,14]).

The \( a_{\text{N+N}} \) factor has been previously [9] determined in conditions of mixed pink and late afterglows (\( a_{\text{N+N}} = 1 \) in pure late afterglow and \( a_{\text{N+N}} = 0 \) in pure pink afterglow) in Ar/x%N\textsubscript{2} gas mixtures with x varying between 2 and 100\%. It is reported in Fig.2 the band intensity ratio \( R = I_11/I_9 \) of the N\textsubscript{2} 1\textsuperscript{+} (11-7) and (9-5) bands versus the \( a_{\text{N+N}} \) factor for He/x%N\textsubscript{2} gas mixtures with x = 10 to 100.

\[
\text{Fig. 2} \ I_11/I_9 \text{ intensity ratio of N}_2 \ 1^+ (11-7) \text{ and (9-5) bands versus the } a_{\text{N+N}} \text{ factor in He/x%N}_2 \text{ gas mixtures with } x=10-100%.
\]

Eq. (1) becomes:

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

In Ar/x%N\textsubscript{2} gas mixtures, it was found a constant value of \( k_1 \) for Ar dilution up to 95\%. It is not the case for He dilution as shown in Fig. 3.

The reported \( k_1 \) value in Fig. 3 is for the optical fibre in front of the 5 litre reactor and for the spectrometer Acton with a 600 gr/mm grating, slit of 0.1 mm, counting time of 1 s.

By detecting in the dia 18 mm tube at z = 50 cm, \( I_{580} \) has to be multiplied by 1.5 (±0.3) to deduce the N-atom density from eq. (1) with the \( k_1 \) values of Fig. 3. Consequently, the \( k_1 \) values in Fig. 3 have to be divided by 1.5 when detecting in the dia.18 mm tube.

It is thus obtained \( k_1 = 0.5 \ (±0.1) \ 10^{26} \ \text{cc cm}^6 \) from \( I_{580} \) intensity measurements in pure N\textsubscript{2} in the dia.1.8 cm tube. This value is in good agreement with the value published in [9]: \( k_1 = 0.6 \ (±0.3) \ 10^{26} \ \text{cc cm}^6 \)
As reported in [15], the $N_2(A)$ and $N_2(X,v>13)$ densities can be deduced from the N-atom density by a line ratio method. It results:

$$a_{N+N} \frac{I_{380}}{I_{316}} = k_2 \left(\frac{[N]}{[N_2(A)]}\right)^2 \quad (3)$$

where it is calculated after N and O-atom density titration by NO [8] that $k_2 = 2.5 \pm 0.5 \times 10^{-7}$ in pure $N_2$, $4 \times 10^{-7}$ in Ar-2%$N_2$ and $2 \times 10^{-7}$ in He-(40-80%$N_2$).

Densities of $N_2(X,v>13)$ vibrational metastable molecules are obtained by the following equation [9] :

$$a_{N+N}/1-a_{N+N} = k_3 \frac{[N]}{[N_2(A)][N_2(X,v>13)]} \quad (4)$$

where it is calculated $k_3 = 7 \times 10^{-6}$ in pure $N_2$ and in Ar-$N_2$ and $k_3 = 3 \times 10^{-6}$ in He/<40%$N_2$.

As it concerns the $N_2^+$ ions, the line ratio intensity is given by the following equation:

$$I_{391}/I_{316} = k_4 \left(\frac{[N_2^+][N_2(X,v>12)]}{[N_2(A)]}\right)^2 \quad (5)$$

with $k_4$ decreases from 8.5 to $4.0 \times 10^{-2}$ in Ar/(20-100%) $N_2$ and from $1.2 \times 10^{-1}$ to $4 \times 10^{-2}$ in He/(20-100%$N_2$) (the $N_2^+(B,0)$ quenching by He is in [16]).

So-obtained densities of N-atoms, of $N_2(A)$ and $N_2(X,v>13)$ metastable molecules and of $N_2^+$ ions are reproduced in Table 1 for the considered R/x%$N_2$ (R=Ar or He) gas mixtures. The uncertainty on the N-atom density is estimated to be ±30%. It is estimated the order of magnitude for the densities of $N_2(A)$, $N_2(X,v>13)$ and $N_2^+$, depending of the rate coefficient values in $k_2$, $k_3$ and $k_4$.

It is deduced from the results in Table 1 that about the same N-atom densities are found in Ar/x%$N_2$ and in He/x%$N_2$ mixed afterglows with $[N] = (1-2) \times 10^{15}$cm$^{-3}$.

Compared with the He/x%$N_2$ gas mixture, the $N_2(A)$ and $N_2(X,v>13)$ metastable molecules densities are higher by a factor 2 in the Ar/<60%$N_2$ gas mixtures. Such a result is well correlated to the observation of a longer plasma column with Ar/x%$N_2$ mixtures compared to He/x%$N_2$, giving a longer residence time for vibrational excitation.
The \( \text{N}_2^+ \) density in pure \( \text{N}_2 \) is in the same order of magnitude of the electron density measured in pink \( \text{N}_2 \) afterglows by microwave interferometry [17] and of the \( \text{N}_2^+ \) density by Langmuir probes [18]. Compared with pure \( \text{N}_2 \), the \( \text{N}_2^+ \) ion density strongly decreases in the \( R/(20-80\%)\text{N}_2 \) gas mixtures.

| Pure \( \text{N}_2 \) | R/80\%\( \text{N}_2 \) | R/60\%\( \text{N}_2 \) | R/40\%\( \text{N}_2 \) | R/20\%\( \text{N}_2 \) |
|------------------|-----------------|-----------------|-----------------|-----------------|
| \( \text{a}_{\text{N}\text{N}} \) (R = Ar) | 0.4 | 0.5 | 0.5 | 0.45 | 0.45 |
| (R = He)         | 0.4 | 0.6 | 0.45 | 0.5 | 0.65 |
| [N] (10^{15} \text{ cm}^{-3}) (R = Ar) | 1.1 | 1.6 | 1.6 | 1.5 | 1.3 |
| (R = He)         | 1.1 | 1.9 | 1.5 | 1.3 | 1.2 |
| [\text{N}_2(A)] (10^{11} \text{ cm}^{-3}) (R = Ar) | 1.2 | 1.3 | 1.3 | 1.3 | 1.1 |
| (R = He)         | 1.2 | 1.2 | 0.8 | 0.7 | 0.5 |
| [\text{N}_2(X,v>13)] (10^{12} \text{ cm}^{-3}) (R = Ar) | 10 | 14 | 13 | 14 | 13 |
| (R = He)         | 10 | 13 | 7  | 7  | 4  |
| [\text{N}_2^+] (10^{9} \text{ cm}^{-3}) (R = Ar) | 4  | 0.6 | 0.5 | 0.4 | 0.1 |
| (R = He)         | 4  | 0.4 | 0.3 | 0.3 | 0.2 |

Table 1 \( \text{a}_{\text{N}\text{N}} \) factors and densities of \( \text{N} \)-atoms, \( \text{N}_2(A) \) and \( \text{N}_2(X,v>13) \) metastable molecules and \( \text{N}_2^+ \) ions in the afterglows of \( R/x\%\text{N}_2 \) gas mixtures with \( R = \text{Ar or He} \) at \( z = 20 \) cm (3 \( \times 10^{-2} \) s) and \( x = 20, 40, 60, 80 \) and 100\% (8 Torr, 1 slm, 150 Watt).

5. Active species densities in Ar/x\%(\text{N}_2-5\%\text{H}_2) and He/x\%(\text{N}_2-5\%\text{H}_2) early afterglows at \( z = 3 \) cm, 8 Torr, 1 slm, 150 Watt.

The pure \( \text{N}_2 \) gas was changed by a \( \text{N}_2-5\%\text{H}_2 \) gas mixture to study the production of \( \text{NH} \) radicals and \( \text{H} \) atoms in addition to the previously determined \( \text{N}_2 \) active species. As indicated in the introduction, the \( \text{NH} \) and \( \text{H} \)-atoms could enhance the surface nitriding as observed in [7,8].

It has been chosen to detect the active species in conditions of early afterglow at \( z = 3 \) cm to expect a high \( \text{H}_2 \) dissociation. The following gas mixtures have been compared: \( \text{N}_2, \text{N}_2/2.5\%\text{H}_2, \text{Ar}/50\%(\text{N}_2-5\%\text{H}_2) \) and \( \text{He}/80\%(\text{N}_2-5\%\text{H}_2) \) at 8 Torr, 1 slm and 150 Watt, \( z = 3 \) cm.

The \( \text{a}_{\text{N}\text{N}} \) factors and active species densities are reported in Table 2.

In the pink afterglow, it has been previously observed a decrease by a factor of about 2 of the \( I_{580} \) intensity half width [12]. Then the afterglow thickness of the N+N recombination part (late afterglow) is lowered by a factor of about 2 and by following eq. (1), the N-atom density has to be multiplied by 1.4. This spatial inhomogeneity of the \( I_{580} \) intensity is taken into account when the pink afterglow is dominant, that is when the \( \text{a}_{\text{N}\text{N}} \) value is lower than 0.5, by multiplying by 1.4 the measured N-atom density. It is the case for the results presently reported as \( \text{a}_{\text{N}\text{N}} = 0.2 \) in \( \text{N}_2 \).

In \( \text{N}_2/2.5\%\text{H}_2 \) and in \( \text{Ar}/50\%(\text{N}_2-5\%\text{H}_2) \), as \( \text{a}_{\text{N}\text{N}} = 0.6-0.7 \) the late afterglow is dominant, conducing to a better homogeneity of \( I_{580} \) and a measured N-atom density without correction.

Densities of \( \text{N}_2(A), \text{N}_2(X,v>13) \) and \( \text{N}_2^+ \) at \( z = 3 \) cm in the \( \text{N}_2, \text{N}_2/2.5\%\text{H}_2, \text{Ar}/50\%(\text{N}_2-5\%\text{H}_2) \) and \( \text{He}/80\%(\text{N}_2-5\%\text{H}_2) \) afterglows at 8 Torr, 1 slm and 150 W are calculated with the rate coefficients \( k_1 - k_5 \) (see part 4.).

The \( \text{N}_2^+ \) ions density is high in pure \( \text{N}_2 \): about 10^{11} \text{ cm}^{-3} with a sharp decrease by a factor 30 between \( z = 3 \) and 20 cm.

The decrease of \( \text{N}_2^+ \) in \( \text{N}_2-2.5\%\text{H}_2 \) is certainly the result of the efficient charge transfer reaction: \( \text{N}_2^+ + \text{H}_2 \rightarrow \text{NH}_2^+ + \text{N} \) with a rate coefficient of 1.7 \( \times 10^9 \) cm^{3}s^{-1} [19].
Table 2  $a_{N+\text{N}}$, factors and $N$, $N_2(A)$, $N_2(X,v>13)$ and $N_2^+$ active species densities determined at $z=3$ cm in the early afterglows of Ar/x%(N$_2$-5%H$_2$) and He/x%(N$_2$-5%H$_2$) gas mixtures (8 Torr, 1 slm and 150W). The $[\text{NH}]$ and $[\text{H}]$ densities are calculated with $N_2(X,v>13)/\text{NH}$ and $N+\text{H}+N_2$ rate coefficients of $5 \times 10^{-11}$ cm$^3$s$^{-1}$ and $5 \times 10^{-12}$ cm$^3$s$^{-1}$ (see text).

6. Density of NH radicals and H-atoms

The kinetic reaction producing the NH(A) radiative state at 330 nm in the afterglows of R/N$_2$/H$_2$ (R = Ar or He) mixtures is unknown. It is presently considered that it can be produced by two reactions: the recombination of N+H atoms or by collisions between vibrationally excited N$_2(X,v>13)$ molecules and NH radicals.

The N+H+M (with M = R(Ar,He)/N$_2$/H$_2$) recombination producing the NH(A,0) excited state is first examined by analogy with the N+O+M recombination process producing the NO(B,0) excited state [20].

The only known rate coefficient corresponds to the 3-body N+H recombination with N$_2$:

$$N + H + N_2 \rightarrow NH + N_2$$

with $k_b = 5(\pm 3) \times 10^{-32}$ cm$^6$ s$^{-1}$ [19].

By considering the NH potential curves [21], the NH(A,v=0) vibrational level and the N+H atoms have about the same energy (3.8-4.0 eV). Moreover, a repulsive NH($^3\Sigma$) potential curve crosses the one of the NH($^2\Pi$) state at 4.2 eV. As a consequence, there is a potential barrier which inhibits the production of NH(A,v=0) by the N+H recombination. The N+H+M → NH(A)+M reaction is thus endothermic.

By comparing with N$_2$/O$_2$ gas mixtures, the potential energy of the NO(B,v=0) level being 0.9 eV lower than the N+O dissociation (6.5 eV), the reaction $N + O + M \rightarrow NO(B,0) + M$ (M = N$_2$/O$_2$) is exothermic.

Considering now the $N_2(X,v) + NH \rightarrow N_2 + NH(A,v=0)$ reaction, the excitation of the NH(A,0) level from the fundamental NH(X,0) level needs 3.8 eV, which corresponds to an exothermic threshold for the reaction with $N_2(X,v>13)$. It is thus estimated that reaction (c) is the most efficient source of NH(A) excitation.
The $I_{336}$ intensity can then be written as follows:

$$I_{336} = c(336) \frac{hc}{336} A(336) \frac{\nu_{RNH(A)} + [M]}{k_{MNH(A)}}$$

where $c(336)$ is the spectral response of the used monochromator modified by the transmission rate of light through the tube at 336 nm, $A(336)$ is the NH(A,0-X,0) vibrational transition probability, $A_{336} = \nu_{RNH(A)} = 2 \times 10^{6}$ s$^{-1}$ [23] and $k_{MNH(A)}$ is the quenching rate of NH(A) by the M molecules. In [23], it is reported that $k_{ArNH(A)} < 9 \times 10^{-14}$ cm$^3$s$^{-1}$, $k_{N2NH(A)} < 5 \times 10^{-14}$ cm$^3$s$^{-1}$ and $k_{H2NH(A)} = 5 \times 10^{-11}$ cm$^3$s$^{-1}$.

Then, the intensity ratio method [15] is applied to determine the NH radical density from the $a_{N+N} I_{580}/I_{336}$ intensity ratio.

It is obtained:

$$a_{N+N} I_{580}/I_{336} = \frac{k_{1}[N]^2}{k_{6}[X,v>13][NH]}$$

where $k_{6} = c(336) \frac{hc}{336} A(336) \frac{\nu_{RNH(A)} + [M]}{k_{MNH(A)}}$

H-atoms and NH densities are related by the following relations:

$$N + H + N_2 \rightarrow NH + N_2$$

with $k_{d} = 5(\pm 3) \times 10^{-32}$ cm$^6$s$^{-1}$ [21]

$$N + NH \rightarrow H + N_2$$

with $k_{e} = 5 \times 10^{-11}$ cm$^3$s$^{-1}$ [20].

In pseudo-stationary conditions, it is considered that H and NH are coupled by reactions (d) and (e).

It comes at 8 Torr, by taking the $k_{d}$ value of $N_{2}$ in the chosen R/N$_{2}$/H$_{2}$ (R = Ar or He) gas mixture where $N_{2}$ is the dominant gas:

$$[NH] = 2.6 \times 10^{-4} [H].$$

The $k_{e}$ rate coefficient has been chosen to be similar to the one of the $N_{2}(X,v>13) + N_{2}(A) \rightarrow N_{2} + N_{2}(B,11)$ and $N_{2}(X,v>13) + N_{2}^{+} \rightarrow N_{2} + N_{2}^{+}(B)$ exothermic reactions [24,25] : $k_{e} = 5 \times 10^{-11}$ cm$^3$s$^{-1}$.

So obtained NH and H densities are reported in Table 2. With the chosen $k_{e}$ value of $5 \times 10^{-11}$ cm$^3$s$^{-1}$, it is obtained more H-atoms in the He/80%(N$_{2}$-5%H$_{2}$) gas mixture.

Appearing to be a rich source of NH radicals and of N and H atoms, R/N$_{2}$/H$_{2}$ (R=Ar or He) afterglows can be of interest for surface treatments, as observed for TiO$_{2}$ layers [8].

7. Conclusion

Early afterglows of R/x%N$_{2}$ and 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 and $N_{2}^{+}$ ions by the line ratio method after calibration of the N-atom density by NO titration. The line intensity ratio method also allowed evaluating the density of NH radicals and H- atoms.
For this estimation, rate coefficients of $5 \times 10^{-11}$ cm$^3$s$^{-1}$ has been considered for the reactions $N_2(X,v>13) + NH$ and $5 \times 10^{-32}$ cm$^6$s$^{-1}$ for $N^+H+M$ where $N_2$ is the dominant gas in $M= R(He, Ar)/N_2/H_2$ gas mixtures.

Such values conduced to a H atom density of about 50 more in a He/80%(N$_2$-5%H$_2$) than in a N$_2$/2.5%H$_2$ early afterglow at 8 Torr, 1 slm, 150 Watt, z = 3 cm (10$^{-3}$ s).

Results are in progress for other He/x%(N$_2$-5%H$_2$) gas mixtures.

The obtained results will indicate the best conditions to produce N and H– atoms in afterglows for specific surface treatments.

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