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Active species in N$_2$ flowing post-discharges

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Abstract. — The afterglow in D.C. and H.F. N$_2$ flowing discharges has been analysed by emission spectroscopy. Production of excited species has been studied in conditions of late $\Delta t = (1-5) \times 10^{-1}$ s and early $\Delta t = (0.5-5) \times 10^{-2}$ s afterglows. The late afterglow is characterized by the N$_2$ 1st positive emission with a strong enhancement of the N$_2$(B, $v'$ = 11) level compared to the other N$_2$(B, $v'$) levels which is a signature of N atom density. By NO titration, we have determined that N/N$_2$ dissociation degrees are respectively 4.1 % and 2.7 % in a 60 W H.F. and in a 50 mA D.C. post-discharge at 4.5 Torr. The early afterglow is characterized by a strong 1st positive emission which has been analysed from the N$_2$(A) + N$_2$(X, $v > 5$) excitation transfer reaction. By introducing a little CH$_4$(10$^{-4}$-10$^{-3}$) or H$_2$(10$^{-2}$ 10$^{-1}$) into the N$_2$ D.C. and H.F. post-discharges, N$_2$(A) quenching rates have been obtained indicating that the N$_2$(A) is only excited on the two first vibrational states in the early afterglows.

1. Introduction.

Production of active species in a flowing post-discharge is studied in connection with plasma reactions for surface treatment. With N$_2$ D.C. and microwave discharges, the N-atom flux in the post-discharge has been previously determined by NO titration and has been correlated to the growing of iron nitrided layers [1]. The post-discharge with N atoms is characterized by a specific yellow afterglow [2], following the reaction:

$$N + N + M_2 \rightarrow N_2(B, 11) + M_2$$

(a)

$$N_2(B, 11) \rightarrow N_2(A, 7) + h\nu(580 \text{ nm}) .$$

The strong enhancement of emission from N$_2$(B, 11) state compared to that of other N$_2$(B, $v'$) levels is the signature of N atoms in the post-discharges which can be easily observed for gas pressures greater than 1 Torr (three body reaction) and for times greater than 0.1 s (late afterglow).

At shorter times and gas pressure 0.1-1 Torr in the post-discharge, other active species such as N$_2$(A) metastable molecules are still sufficiently numerous to produce specific reactions.

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It is the purpose of the present paper to report the results of the emission spectroscopy in the late and early N\textsubscript{2} afterglows. The comparison of N-atom production has been realized between D.C. and microwave discharges. The effect on the N\textsubscript{2} excited states of adding small CH\textsubscript{4} and H\textsubscript{2} percentages to N\textsubscript{2} is specifically studied.

2. The experimental set-up.

The experimental set-up is reproduced in figure 1. Several discharge configurations have been arranged in pyrex tubes of diameters 2 cm and 0.4 cm.

A positive column can be produced between side-armed anode (A) and cathode (K) 30 cm apart along the tube of diameter 2 cm. Microwave discharges can be independently produced in tubes of diameter 2 cm and 0.4 cm, by using a surfatron launcher [3]. The tube diameters have been chosen to allow the comparison with previous results in D.C. (diameter 2 cm) and in microwave (0.4 cm) N\textsubscript{2} post-discharge reactors [1]. In the experimental set-up of figure 1, the NO gas can be introduced at the beginning of the post-discharge tube for N-atom titration. The post-discharge tube of diameter 5.6 cm is connected to a 400 m\textsuperscript{3}/h Roots pump system by means of a throttle valve. The gas pressure and flow-rates are measured with an absolute gauge and mass flowmeter controls, respectively:

The residence time (\(\Delta t\)) in the post-discharge is deduced from the values of gas pressure (\(p\)) and standard flow rate (\(Q_0\)) at room gas temperature (300 K) : 

\[ \Delta t = \frac{\pi R^2 Z p_0}{Q_0 p} \]

where \(R\) is the tube radius, \(Z\) distance between the discharge end and the observation area and \(p_0\) the atmospheric gas pressure.

The afterglow is analysed by emission spectroscopy using a Jobin-Yvon HR640 spectrometer equipped with a 1 200 grooves per mm diffraction grating and a Hamamatsu R928 photomultiplier, connected to a photon counting and a computer controlling system.

3. Production of N atoms in the late afterglow : 

In conditions of N\textsubscript{2} or Ar-N\textsubscript{2} late afterglow, the 1st positive emission has been recorded and is reproduced in figure 2 for a H.F. (60 W, dia. 0.4 cm) Ar-10 % N\textsubscript{2}, post-discharge at 4.5 Torr and a time of \(\Delta t = 0.3 \text{ s}\). By introducing NO into the post-discharge, the N\textsubscript{2} dissociation
degree which is obtained after extinction of NO\(_b\) bands and before the NO\(_2\) continuum appears [1, 2] has been determined at the null point.

It has been found \(\frac{[N]}{[N_2]}\) = 2.7\% in the D.C. Ar-10\% N\(_2\) post-discharge at 4.5 Torr and 50 mA in the positive column \((R = 1 \text{ cm})\) where the electric field and the power can be estimated to be 50 V/cm\(^{-1}\) [4] and 75 W, respectively. With the H.F. 1 000 MHz Ar-10\% N\(_2\) discharges at 4.5 Torr and 60 W, the dissociation degree is higher: \(\frac{[N]}{[N_2]}\) = 4.1 and 4.3\% after the discharge tubes of diameter 2 cm and 0.4 cm.

The uncertainty of N-atom density measured by NO titration is about 20\%. The gas pressure is limited to about 5 Torr in the present post-discharge tube (dia. 5.6 cm). In these conditions, the CN-violet band emissions were not detected when a little CH\(_4\) \((10^{-4}-10^{-3})\) was added to the N\(_2\) and Ar-N\(_2\) post-discharges as previously reported [5]. The CN emission results from C + N recombination reactions, the carbon atoms are produced either by olefins in impurity [5] or by introduction of \(10^{-3}-10^{-4}\) CH\(_4\) into N\(_2\) [6] in HF post-discharges, for pressures in the range 10-100 Torr.

In the present Ar-N\(_2\) H.F. post-discharge at 4.5 Torr, 60 W, the pink afterglow is observed at time \(\Delta t = 10^{-1}\) s, just before the late afterglow. The pink afterglow is characterized by a strong intensity of N\(_2^+\) first negative bands as analysed in reference [7]. At shorter times \(\Delta t = 10^{-2}\) s in the case of the 4.5 Torr post-discharge, the early afterglow is characterized by strong intensity of the N\(_2\) first positive bands without N\(_2^+\) first negative emission. Such an early afterglow is observed alone with a strong intensity at low gas pressures (0.2-0.5 Torr) and short residence times \((5 \times 10^{-3}-5 \times 10^{-2}\) s).

4. Active species in the early afterglow: \(\Delta t = (0.5-5) \times 10^{-2}\) s.

The first positive emission in the Ar-10\% N\(_2\) early afterglow of the H.F. discharge (dia. 0.4 cm, \(\Delta t = 2 \times 10^{-2}\) s, \(p = 0.4\) Torr) is reproduced in figure 3 for the same spectral range as in figure 2. By comparing with the spectrum in the late afterglow (Fig. 2), it can be observed
that the (11-7) band is no longer dominant and that the vibrational bands \( N_2(B, v' < 11) \) are well excited. The \( [N_2(B, v')] \) vibrational densities are calculated in relative units from the following equation:

\[
I_{BA}(v', v'') = \frac{C(\lambda) \cdot A_{v', v''}}{A_{v', v''}} \cdot [N_2(B, v')]
\]

where \( C(\lambda) \) is the spectral response of the optical spectrometer, which has been calibrated by use of a tungsten lamp and \( A_{v', v''} \) is the radiative emission probability [8]. The \( [N_2(B, v')] \) vibrational distributions are reproduced in figure 4 for the Ar-10 \% \( N_2 \) H.F. post-discharges at times \( \Delta t = 5 \times 10^{-3} \) s-2 \( \times 10^{-2} \) s and \( p = 0.4 \) Torr in (A) and at time \( \Delta t = 0.3 \) s and \( p = 4.5 \) Torr in (B). The curve (C) in figure 4 is deduced from the \( N_2(B, v') \) densities published in reference [9] where the \( N_2(B, v') \) states are mainly populated by the transfer of electronic energy from \( N_2(A) \) to \( N_2(X, v > 5) \) as:

\[
N_2(A) + N_2(X, v > 5) \rightarrow N_2(X) + N_2(B, v')
\]

with \( k_b = (3 \pm 1.5) \times 10^{-11} \) cm\(^3\)/s [9].

The (A) (B) and (C) vibrational distributions in figure 4 have been normalized with \( [N_2(B, 7)] = 3 \times 10^4 \) cm\(^{-3}\) as reported in reference [9]. The \( N_2(B, 11) \) peak decreases, relatively to other \( N_2(B, v') \), in going from the late to the early afterglow. The (B) distribution has been multiplied by 25 to be compared to the (A) distribution.

The shape of the (A) and (C) distributions are about the same as it concerns the disappearance of the \( N_2(B, 11) \) maximum. Also it can be estimated that the present early afterglow at times \( \Delta t = (0.5-2) \times 10^{-2} \) s is mainly produced by reaction (b). Consequently, the \( N_2(B, v') \) densities can be written as:

\[
[N_2(B, v')] = \frac{[N_2(A)] \cdot [N_2(X, v > 5)] \cdot k_b}{v'_v + [M_2] \cdot k_{Q, v}}
\]
where the radiative frequency $\nu_1' = 1.5 \times 10^5 \text{ s}^{-1}$ [8] and the $k_Q$ quenching rates by Ar, N$_2$, H$_2$ and CH$_4$ are (in cm$^3$/s): $2 \times 10^{-12}$ [2], $3 \times 10^{-11}$ [2], $5 \times 10^{-11}$ [10] and $3 \times 10^{-10}$ [11], respectively.

The introduction of small densities of CH$_4$ in the N$_2$ D.C. post-discharge (0.5 Torr, 50 mA) leads to a decrease of $I_{BA}(v',v'')$ intensities without changing the N$_2$(B, $v'$) vibrational distribution as reproduced in figure 5a for bands at the origin of N$_2$(B, $v'$ = 2 and 12). This decrease cannot be explained by the N$_2$(B, $v'$) quenching in equation (2) since [CH$_4$] $< 3 \times 10^{13} \text{ cm}^{-3}$ and then [CH$_4$] $k_Q < 10^3 \text{ s}^{-1}$ is more than one order of magnitude lower than $\nu_1'$. The quenching of N$_2$(A) and N$_2$(X, $v$) by CH$_4$ is now considered:

$$N_2(A) + CH_4 \rightarrow \text{products} \quad (c)$$

$$N_2(X, v > 5) + CH_4 \rightarrow \text{products} \quad (d)$$

Fig. 4. — N$_2$, 1st pos. vibrational distributions in post-discharges A: early afterglow, Ar-10% N$_2$, 0.4 Torr; B: late afterglow, Ar-10% N$_2$, 4.5 Torr and C: afterglow of a 60 W microwave discharge [9] (the two black triangles for $v' = 4$ and 6 are deduced from vibrational sequences $\Delta V = 2, 3$ and $\Delta V = 3, 4$, respectively).

\[
[B, V'][\text{a.u}]
\]

10^1

1

2

3

4

5

6

7

8

9

10

11

12

\[
V'
\]

\[
A[\Delta -25W - 5 \times 10^{-2}s]
\]

\[
\Delta -40W - 5 \times 10^{-2}s
\]

\[
B[ \times 25]
\]

\[
C[ \text{ref. 9}]
\]
One can derive that \( N_2(B, \nu') \) is related to \( N_2(A) \) and \( N_2(X, \nu > 5) \) by:

\[
[N_2(B, \nu')] = k(\nu') \cdot \exp - (\nu^A + k_c[CH_4]) \Delta t \times \exp - (\nu^X + k_d[CH_4]) \Delta t
\]  

(3)

where

\[
k(\nu') = \frac{[N_2(A)]_0 [N_2(X, \nu > 5)]}{\nu_v^A} \] 

(2)

where \( \nu^A, \nu^X \) frequencies represent the destructions, by reaction (b), by reaction with \( N \) atoms for \( N_2(A) \) molecules and by diffusion on the tube wall \( (\nu^A$, \( \nu^X) \).

- \( \nu^A_w = \frac{\left(D_A \rho\right)}{A^2 \rho} \left(D_A \text{ diffusion coefficient of } N_2(A) \right) \) and \( A \) the diffusion length is \( R/2.4 \) for a tube of radius \( R \).

- \( \nu^X_w = \frac{\gamma}{2 R} \), \( \gamma \), is the wall destruction probability of \( N_2(X, \nu > 5) \) and \( \bar{V} \) is the mean velocity of molecules [4].

- \( k_c \) and \( k_d \) are the quenching rates of reactions (c) and (d), respectively.

As a result of low \( k_d \) quenching rate : \( k_d = 10^{-14} \text{ cm}^3 \text{ S}^{-1} \) [11], it can be calculated that \( \nu^X_w = k_d[CH_4] \) in equation (3) for \( [CH_4] < 3 \times 10^{12} \text{ cm}^{-3} \) and for \( \gamma, = 6 \times 10^{-4} - 6 \times 10^{-3} \) as reported in references [15] and [16]. Also, equation (3) can be simplified as:

\[
[N_2(B, \nu')] = k(\nu') \exp - (\nu^A + \nu^X + k_c[CH_4]) \Delta t
\]  

(4)

The \( k_c \)-rate coefficient can be determined from the slope of \( I_{BA}(\nu', \nu'') \) in log unit versus \( CH_4 \) in figure 5a. From several experiments in \( N_2 \) and \( Ar-10 \% \) \( N_2 \) D.C. and H.F. post-discharges, it has been obtained \( k_c = 1.6 (\pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \). Such a value is well related to \( k_c[A, \nu' = 1, 2] \) published values: \( k_c[A, \nu' = 1] = 1.2 \times 10^{-12} \) and \( k_c[A, \nu' = 6] = 5.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) [13], the \( k_c[A, \nu' = 0] \) being largely lower: \( k_c[A, \nu' = 0] = 3.2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) [12].

With \( H_2 \) in the \( N_2 \) D.C. and M.H. post-discharges, it was necessary to introduce higher quantity of \( H_2 \) to produce a significant decrease of \( I_{BA} \) as indicated in figure 5b for D.C. \( (0.5 \text{ Torr}, 50 \text{ mA}) \). The exponential decay is only obtained for \( [H_2] > 10^{15} \text{ cm}^{-3} \) where the \( N_2(B, \nu') \) density is given by an equation which is similar to equation (3), as:

\[
[N_2(B, \nu')] = k(\nu') \exp - (\nu^A + k_c[H_2]) \Delta t \times \exp - (\nu^X + k_d[H_2]) \Delta t
\]  

(5)

where the \( k_c \) and \( k_d \) rate coefficients are for the following reactions:

\[
N_2(A) + H_2 \rightarrow \text{products}
\]  

(e)

\[
N_2(X, \nu > 5) + H_2 \rightarrow \text{products}
\]  

(f)

In equation (5), \( k(\nu') \) is decreasing with \( H_2 \) density as a result of \( N_2(B, \nu') \) quenching (see Eq. (2)). This effect has been taken into account in the decay of \( I_{BA} \) in figure 5b. By taking the \( k_d \) published value: \( k_d = 2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) [11], it has been determined a \( k_c \)-value of \( 4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \). From several experimental sets in \( N_2 \) and \( Ar-10 \% \) \( N_2 \) D.C. and H.F. post-discharges, the \( k_c \)-rate constants are in the \( 10^{-15}-10^{-14} \text{ cm}^3 \text{ s}^{-1} \). By comparing with the \( k_c[A, \nu' = 0] \) published values: \( k_c[A, \nu' = 0] = 2 \times 10^{-15}, k_c[A, \nu' = 1] = 4 \times 10^{-14} \) [12, 14], \( k_c[A, \nu' = 2] = 6 \times 10^{-14} \) and \( k_c[A, \nu' = 6] = 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) [13], the \( k_c \) values presently found indicate a quenching of \( N_2(A, \nu' = 0, 1) \).

The initial sharp decay of \( I_{BA} \) observed in figure 5b could be the result of an increase of \( \nu^A + \nu^X \) in equation (5). A sharp increase of \( N \) atom density in \( N_2 + (1-3 \%) \) \( H_2 \) afterglow [16]
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Fig. 5. — N₂, 1st post relative intensities versus CH₄ (a) and H₂ (b) in D.C. N₂ post-discharge (0.5 Torr, 50 mA).

has been recently observed. This effect in the present early afterglow should increase $\nu^A$ by the N₂(A) + N reaction.

5. Conclusion.

The kinetics reactions of active species in N₂ D.C. and H.F. post-discharges have been studied from emission spectroscopy. The late and early afterglows have been analysed in Ar-10 % N₂ at mean gas pressures of 4.5 and 0.4 Torr, respectively. In the 4.5 Torr late afterglow at time of 0.3 s, the N/N₂ dissociation degree was slightly higher after microwave discharges at 60 W, $R = 1$ cm (4.1 %) as compared to a positive column at $I = 50$ mA (~75 W), $R = 1$ cm (2.7 %).

An early afterglow has been detected in the range $(0.5-5) \times 10^{-2} s$ which mainly results from the excitation transfer: N₂(A) + N₂(X, $\nu > 5$) $\rightarrow$ N₂ + N₂(B, $\nu'$). The addition of
CH$_4$ or H$_2$ in the N$_2$ post-discharge reduces the N$_2$(B, v') production by quenching of N$_2$(A) molecules. The N$_2$(A) + (CH$_4$, H$_2$) quenching rates are $(1.6 \pm 0.4) \times 10^{-12}$ and $10^{-15}$-$10^{-14}$ cm$^3$/s respectively. By comparing with published values it is deduced that the N$_2$(A, v') molecules are weakly excited in the D.C. and H.F. post-discharges at levels $v' < 2$.

References