Determination of N and O-Atoms, of $\text{N}_2(A)$ and $\text{N}_2(X, v > 13)$ Metastable Molecules and $\text{N}_2^+$ Ion Densities in the Afterglows of Ar-N$_2$ Microwave Discharges

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Abstract

Early afterglows of Ar-N$_2$ flowing microwave discharges are characterized by optical emission spectroscopy. The N and O atoms, the $\text{N}_2(A)$ and $\text{N}_2(X, v > 13)$ metastable molecules and $\text{N}_2^+$ ion densities are determined by optical emission spectroscopy after calibration by NO titration for N and O-atoms and measurements of NO and $\text{N}_2$ band intensities. For an Ar-xN$_2$ gas mixture with x increasing from 2 to 100% at 4 Torr, 100 Watt and an afterglow time of $3 \times 10^{-3}$ s at the 5 liter reactor inlet, it is found densities in the ranges of $(2 - 6) \times 10^{14}$ cm$^{-3}$ for N-atoms, one order of magnitude lower for $\text{N}_2(X, v > 13)$ and for O-atoms (coming from air impurity), of $10^{10} - 10^{11}$ cm$^{-3}$ for $\text{N}_2(A)$ and of $10^8 - 10^9$ cm$^{-3}$ for $\text{N}_2^+$. 

Keywords

Ar-N$_2$ Microwave Discharge, Flowing Afterglow, N-Atoms, $\text{N}_2$ Metastables, $\text{N}_2^+$ Ions

1. Introduction

Afterglows of $\text{N}_2$ flowing microwave discharges have been studied at medium gas pressures (1 - 20 Torr) for sterilization of medical instruments by N-atoms [1] [2]. The mentioned project of sterilization in $\text{N}_2$ afterglow is based on N-atom etching of bacteria without oxidation by O-atoms. A part of the present study is to detect the O-atoms from air impurity to appreciate their influence on the sterilization process.

The main part concerns a study of Ar-N$_2$ gas mixtures to enhance the sterilization process in the early after-
The interest of $N_2$ dilution into Ar is 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 could enhance the electron energy. It is mentioned here that in the present measurements of flowing afterglow, the Ar metastable atoms have disappeared after collisions on the tube wall (destruction probability of about 1). As a consequence, the excitation transfers of Ar metastable atoms on $N_2$ can be discarded at a distance of about 1 cm after the discharge end. Another interest of Argon dilution is 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 early flowing afterglows produced from Ar-$N_2$ microwave plasmas are presently studied by emission spectroscopy with the same experimental methods as in $N_2$-H$_2$ RF afterglow [4] [5], in $N_2$, $N_2$-O$_2$ [6] and in $N_2$-H$_2$, Ar-$N_2$-H$_2$, Ar-$N_2$-O$_2$ microwave early afterglows [6].

The present paper is focused on Ar-$N_2$ early afterglow by directly introducing the discharge tube of 5 mm dia. inside the 5 litre reactor. By this way, it is expected to add the metastable $N_2(A)$ and $N_2(X, v > 13)$ molecules and $N_1^+$ ions to the N-atoms in the surface treatments as previously experimented [1] [2]. The studied active species are as in [6] the N and O-atoms, the $N_2(A)$ and $N_2(X, v > 13)$ metastable molecules and $N_1^+$ ions. The intensities emitted by the $N_2$ first positive (1st pos.) and $N_2$ second positive (2nd pos.) systems and by the NO $\beta$ bands are measured to obtain the mentioned active specie densities after NO titration to calibrate the N and O-atom densities [6]. The O-atoms are coming from air impurity in the discharge.

2. Experimental Setup and NO Titration

The experimental setup is changed in comparison to the one used in [6]. The dia. 5 mm discharge tube is now directly connected to the 5 litre reactor as shown in Figure 1. The Ar-$N_2$ microwave plasmas are always produced by a surfatron cavity at 2450 MHz, 100 Watt, 1 slm, but lowering the gas pressure from 8 Torr in [6] to 4 Torr to allow a satisfactory 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 before the afterglow in the 5 litre reactor is $3 \times 10^{-3}$ s.

The optical emission spectroscopy across the 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 × 256 pixels).

The N-atom density is obtained from the $I_{580}$ measured intensity after calibration by NO titration as described in [6].
3. The Ar-N₂ Early Afterglow

3.1. N-Atom Density

As reported in [6], the pure late afterglow emission is produced by reaction R1 in Table 1.

The N₂ (580 nm) band head intensity ($I_{580}^m$) in arbitrary unit (a.u) was measured for constant parameters of the Acton spectrometer (grating 600 gr/mm, slit of 150 μm, integrating time 1 s).

$I_{580}^m$ is then deduced from reaction R1 with $v' = 11$ and $hυ = hc/λ$ (580 nm), as follows:

$$I_{580}^m = k_1[N]^2$$  \hspace{1cm} (1)

with $k_1$ explicited in [4]-[6].

The reaction R1 produced with an excess of Ar atoms results in a change of the N₂(B, $v'$) distribution as compared to pure N₂ at a given $a_{N+N}$ value. The N + N recombination coefficient $a_{N+N}$ has been calculated in [6] in conditions of pink and late afterglows for Ar-xN₂ gas mixture with x from 2% to 100%.

Equation (1) becomes:

$$a_{N+N}I_{580}^m = k_1[N]^2$$  \hspace{1cm} (2)

By NO titration, it has been verified the same $k_1$ value inside the error bars as for pure N₂ [6]: $k_1 = 0.6 (+/-0.3) 10^{-26}$ cm$^6$ counts/s with $I_{580}^m$ in counts/s and [N] in cm$^{-3}$.

It is obtained $a_{N+N} = 0.9$ for pure N₂ and $a_{N+N} = 0.5$ for the Ar-2% N₂ mixture in the 5 litre reactor.

This result indicates that the early afterglow in N₂ is dominated by the N+N recombination as expressed by R1.

The N-atom density is then obtained in the 5 litre reactor by taking into account the change of diameter from 2.1 cm in the tube to 15 cm in the reactor.

It is reported in Figure 2 the N-atom density variation with the %N₂ into Ar

A slow increase of N-atom density is found in the range 2% - 10% N₂ to reach a constant value of $5 - 6 \times 10^{14}$ cm$^{-3}$ between 10 and 100% N₂. The uncertainty on N-atom density is estimated to be 30% [6].

Table 1. Kinetic reactions in Ar-N₂ afterglow.

<table>
<thead>
<tr>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>N + N + (Ar-N₂) → N₂(B, v') + (Ar-N₂)</td>
</tr>
<tr>
<td>N₂(B, v') → N₂(A, v') + hυ_{B(580)}</td>
</tr>
<tr>
<td>N + O + (Ar-N₂) → NO(B, 0) + (Ar-N₂)</td>
</tr>
<tr>
<td>NO(B, 0) → NO(X, 8) + hυ_{580 nm}</td>
</tr>
<tr>
<td>N₂(A) + N₂(A) → N₂(C, I) + N₂(X)</td>
</tr>
<tr>
<td>N₂(C, I) → N₂(B, 0) + hυ_{316 nm}</td>
</tr>
<tr>
<td>N₂(A) + N₂(A) → N₂(B, 11) + N₂</td>
</tr>
<tr>
<td>N₂(A) + N₂(X, v &gt; 13) → N₂(B, 11) + N₂</td>
</tr>
<tr>
<td>N₂(a') + N₂(a') → e + N₂(X) + N₂(X)</td>
</tr>
<tr>
<td>N₂(X) + N₂(X &gt; 12) → N₂(B) + N₂(X)</td>
</tr>
<tr>
<td>N₂(B, 0) → N₂(X, 0) + hυ_{391 nm}</td>
</tr>
<tr>
<td>Ar⁻ + N₂ → Ar + N₂</td>
</tr>
</tbody>
</table>
3.2. Density of O-Atoms in Impurity in the Ar-N₂ Early Afterglow

The NO₂ bands are presently observed as a result of the recombination of N and O atoms by reaction R2. In a similar way than for Equation (1), the NO (320 nm) measured band intensity ($I_{320}^m$) is deduced from reaction R2 as follows:

$$I_{320}^m = k_3 [N][O]$$

(3)

The coefficients in $k_3$ are explicited in ref. 6 as for $k_1$.

The O atom density can be deduced from the N-atom density by considering the $N+N$ ratio of reactions 2 and 3, as follows:

$$a_{NN} \cdot \frac{I_{320}^m}{I_{580}^m} = k_4 [N]/[O]$$

(4)

with $k_4 = k_1/k_3$.

After several NO titration experiments, it was found in [6]: $k_4 = 1(+/−0.4)$. From $k_4$ obtained by NO titration, the O-atom density in the Ar-N₂ early afterglow inside the reactor was determined by Equation (4) after measurements of $a_{NN} \cdot \frac{I_{580}^m}{I_{320}^m}$ and $[N]$ versus the N₂ percent into Ar. The results are reproduced in Figure 2. If the uncertainty on N-atom density is estimated to be 30% (see part 3.1), the experimental errors on O-atom density calculated from Equation (4), with the uncertainty on $k_4$ of 40% is 90% that is near the order of magnitude.

As shown in Figure 2, there is a slow decrease of the O-atom density from 3 to $2 \times 10^{13}$ cm$^{-3}$ between 2% to 100% N₂.

3.3. Density of N₂(A) Metastable Molecules

It has been detected the N₂(C, 1→B, 0) emission at 316 nm near the NO₂ emission at 320 nm which is used as in [4]-[6] to determine the density of the N₂(A) metastable molecule.

It is considered that the N₂ 2$^\text{nd}$ positive system in the early afterglow is produced by reaction R3.

The N₂ (316 nm) measured intensity ($I_{316}^m$) is then given by:

$$I_{316}^m = k_5 \left[ N_2(A) \right]^2$$

(5)

with $k_5$ explicited in [6].

From Equations (3) and (5), it comes the following $I_{320}^m/I_{316}^m$ intensity ratio:
with \( k_6 = k_2/k_4 \). The \( N_2(A) \) density is then obtained from equation (6) with the N and O atom densities previously determined.

As shown in Figure 2, the \( N_2(A) \) density kept a constant value in the Ar-N\(_2\) gas mixture. It is estimated that it is obtained the order of magnitude of \( N_2(A) \) density in the range \( 10^{10} - 10^{11} \text{ cm}^{-3} \).

### 3.4. Density of \( N_2(X, v > 13) \) Molecules

The production of \( N_2(B, 11) \) by R1 in the early afterglow is less than 1 ( \( a_{N+N} < 1 \)).

Other collisional processes in the pink afterglow [7] also excite the \( N_2(B) \) states, in addition to reaction R1.

For this other part \( (1 - a_{N+N}) \), it is considered the reactions R4 and R5 whose rate coefficients are reported in [4]-[6]. The contribution of reactions R4 and R5 on \( I_{580}^m \) is then written as follows:

\[
(1 - a_{N+N}) I_{580}^m = k_{R4} \left[ N_2(A) \right]^2 + k_{R5} \left[ N_2(A) \right] \left[ N_2(X, v > 13) \right]
\]

Where \( k_{R4}, k_{R5} \) are the rate coefficients of reactions R4, R5. As \( a_{N+N} I_{580}^m = k_1 \left[ N \right]^2 \), it is deduced:

\[
(1 - a_{N+N}) (k_{R4} \left[ N_2(A) \right]^2 + k_{R5} \left[ N_2(A) \right] \left[ N_2(X, v > 13) \right]) = \left[ N \right]^2 k_1
\]

With the experimental values of \( a_{N+N} \) and of N and \( N_2(A) \) densities, it is found that \( (a_{N+N}/1 - a_{N+N}) k_{R4} \left[ A \right]^2 \) is about 2 orders of magnitude lower than \( \left[ N \right]^2 k_1 \). It results that Equation 8 can be simplified as:

\[
(a_{N+N}/1 - a_{N+N}) k_{R5} \left[ N_2(A) \right] \left[ N_2(X, v > 13) \right] = \left[ N \right]^2 k_1
\]

From the obtained values of N-atom and \( N_2(A) \) density, it was deduced the values of \( [N_2(X, v > 13)] \) as reproduced in Figure 2.

It is observed about one order of magnitude lower \( N_2(X, v > 13) \) density as compared to N values.

Such values of \( [N_2(X, v > 13)] \) can be considered as an estimated value depending on the R5 rate coefficient.

### 3.5. Density of \( N_2^+ \) Ions

The emission of the \( N_2^+ \) band at 391 nm is observed in the present early afterglows. It is generally proposed [8] that the \( N_2^+, 391 \text{ nm} \) band is produced in the pink afterglow by reactions R6 and R7.

The \( I_{391}^m \) intensity is then expressed as follows:

\[
I_{391}^m = k_{10} \left[ N_2^+ \right] \left[ N_2(X, v > 12) \right]
\]

Where \( k_{10} = c_{391} \cdot V \cdot A_{391} \cdot k_{R7} / \left( v_{N_2}^p + \left[ N_2 \right] k_{NIB,0}^0 \right) \), where \( c_{391} \) is the spectral response of spectrometer, V is the detected afterglow volume, \( A_{391} \) the Einstein coefficient of the \( N_2^+ \) (391 nm) transition, \( k_{R7} \) the rate coefficient of reaction R7 with \( k_{R7} = 4 \times 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1} \) [9], \( v_{N_2}^p = 1.7 \times 10^7 \text{ s}^{-1} \) and \( k_{NIB,0}^0 = 8.8 \times 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1} \) [10].

By comparing the intensities of \( I_{316}^m \) from Equation (5) and \( I_{391}^m \) from equation (10), it is calculated:

\[
I_{391} / I_{316} = k_{11} \left( \left[ N_2^+ \right] \left[ N_2(X, v > 12) \right] / \left[ N_2(A) \right]^2 \right)
\]

Where \( k_{11} \) increasing from 6.6 \( 10^{-2} \) in pure \( N_2 \) to 0.17 in Ar-2\%\( N_2 \).

By assuming the equality \( [N_2, X, v > 12] = [N_2, X, v > 13] \), it is found a \( N_2^+ \) density which decreases from about \( 10^9 \text{ cm}^{-3} \) in pure \( N_2 \) to \( 2 \times 10^8 \text{ cm}^{-3} \) in Ar-10\%\( N_2 \) and increases again to \( 10^9 \text{ cm}^{-3} \) in Ar-2\%\( N_2 \). To verify that the \( N_2^+ \) ions are not coming from the end of a plasma jet at Ar-2\%\( N_2 \), the measurements have also be performed 5 cm above in the 5 litre reactor, keeping about the same results.

Compared to published data [11] [12], the value of \( N_2^+ \) density in pure \( N_2 \) appears to be in the same order of magnitude.

### 4. Interest of Ar-N\(_2\) Gas Mixture for Surface Treatments

It is reported in Figure 3 the \( N/N_2, N_2(X, v > 13)/N_2, N_2(A)/N_2 \) and \( N_2^+ / N_2 \) density ratio versus the \%\( N_2 \) into
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Figure 3. Density ratios of active species on \( N_2 \) versus the %\( N_2 \) in the Ar-N\( _2 \) gas mixtures. In addition \( \frac{[N_2]}{[N_2]} \) ratio.

Ar. Clearly, there is an interest of low %\( N_2 \) to increase the active species density relative to \( N_2 \) if it can be considered that the Ar atoms have no influence on the surface processes.

The \( \frac{[N_2]}{[N_2]} \) density ratio is nearly constant from pure \( N_2 \) to Ar-10%\( N_2 \) with a new increase with Ar-2%\( N_2 \).

There is thus an interest of Ar-x\( N_2 \) gas mixtures with x = 2% - 20% for surface treatments with high \( N_2(A, X_v > 13) \) and \( \frac{[N_2]}{[N_2]} \) density values (see Figure 2).

The \( \frac{[N_2]}{[N]} \) density ratio decreased from pure \( N_2 \) to Ar-10%\( N_2 \) with an increase at Ar-2%\( N_2 \) to find again the value in pure \( N_2 \).

This increase of \( \frac{[N_2]}{[N]} \) density for Ar-2%\( N_2 \) could be the result of the charge transfer R8 at the benefit of the \( \frac{[N_2]}{[N]} \) ions [13].

5. Conclusions

Densities of \( N \) and \( O \) atoms (the \( O \)-are coming from air impurity), \( N_2(A) \) and \( N_2(X, v > 13) \) metastable molecules and \( \frac{[N]}{[N_2]} \) ions have been determined in Ar-N\( _2 \) early afterglows of flowing microwave discharges at 1 slm, 4 Torr, afterglow time of \( 3 \times 10^{-3} \) s and 100 W, after NO calibration.

The density of these active species are obtained by comparing the \( N_2 \) (580 nm), NO\( _{\beta} \) (320 nm), \( N_2 \) (316 nm) and \( \frac{[N]}{[N_2]} \) (391 nm) band intensities and by writing the dominant kinetic equations.

It is found densities in the ranges of \( (2 - 6) \times 10^{14} \) cm\(^{-3} \) for \( \frac{[N]}{[N_2]} \)-atoms, one order of magnitude lower for both \( \frac{[N_2]}{[N_2]}(X, v > 13) \) and \( \frac{[N]}{[N_2]} \)-atoms (coming from air impurity), of \( 10^{10} - 10^{11} \) cm\(^{-3} \) for \( \frac{[N]}{[N_2]} \) and of \( 10^{8} - 10^{9} \) cm\(^{-3} \) for \( \frac{[N]}{[N_2]} \).

The densities obtained by these line-ratio measurements are with an uncertainty of 30% for \( \frac{[N]}{[N_2]} \)-atoms and the order of magnitude for \( \frac{[N]}{[N_2]} \) and \( \frac{[N_2]}{[N_2]}(A) \) metastable molecules. Estimated densities values are obtained for the \( \frac{[N_2]}{[N]}(X, v > 13) \) metastable and \( \frac{[N_2]}{[N]} \)-ions which are depending on the kinetics reaction rates.

It is found that the main interest of \( N_2 \) dilution into Ar is to increase the \( \frac{[N]}{[N_2]} \) dissociation from 0.5% in \( N_2 \) to about 10% in the Ar-2%\( N_2 \) which could be of interest for surface reactions of \( N \)-atoms with less \( N_2 \) molecules.

The other \( \frac{[N]}{[N_2]} \), \( \frac{[N_2]}{[N_2]}(X, v > 13)/[N_2] \) density ratios are also increasing at low %\( N_2 \) into Ar. It is not the case for the \( \frac{[N]}{[N_2]} \) and \( \frac{[N]}{[N_2]} \) ratios which are constant or decreasing from pure \( N_2 \) up to 10%\( N_2 \).
References


