On the oxygen addition into nitrogen post-discharges

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Abstract
It is well known that the dissociation degree of nitrogen can be substantially increased if a small amount of oxygen is added into an active discharge. In this work it is experimentally shown that a very similar phenomenon occurs also when oxygen is added into the nitrogen late post-discharge. A detailed kinetic model, valid for the oxygen addition into the active discharge, fails to interpret these new experimental observations, and, consequently, its completeness has to be questioned.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nitrogen discharges and their afterglows have been intensively studied since the beginning of discharge physics research [1]. Despite this long interest, there are still various open questions in the understanding of N_2 kinetics, and even rather well-known phenomena were recently reinvestigated using up-to-date experimental and theoretical methods. As a result, some formerly well-established explanations were questioned and revised. For example, there is currently an intense discussion concerning the processes ruling the nitrogen pink afterglow [2] as well as the nitrogen dissociation mechanisms at low pressures [3].

The mixtures of nitrogen with other gases present another scientific challenge. The mixture with oxygen is one of the most common. The related research resulted in the development of many commercial and industrial applications, such as the water treatment by ozone [4], plasma surface modification [5] and plasma sterilization [6, 7]. Moreover, the plasma chemical processes in N_2–O_2 mixtures are crucial in the physics of the upper atmosphere, with associated global consequences such as the ozone layer depletion, acid rains and the greenhouse effect [8].

Mixtures with more than several percent of oxygen, such as air, are quite well understood and reliable kinetic models

exist [9, 10]. In contrast, the mixtures with O_2 content lower than 1% have a surprisingly more complicated kinetics, which is subject to much more doubt and discussion. As a matter of fact, oxygen strongly quenches both the electronic excited states of nitrogen and the vibrational manifold of ground-state N_2 molecules, making the overall kinetics relatively simpler as long as the O_2 fraction is not too small [11]. Despite this fact and of the economy of using simply air, in many practical applications mixtures with a low oxygen/nitrogen ratio are advantageous for a given purpose. In these mixtures there are still unresolved kinetic issues and further investigation is needed. One striking occurrence is that when a small amount of O_2 is added into a N_2 discharge, a strong increase in the N atom density is observed in the afterglow [12–14]. In an extreme case, an increase of nearly two orders of magnitude was measured [15]. Several hypotheses explaining this effect were suggested in the literature [9, 12, 16], and will be discussed below.

Although the interpretation of the increase in the nitrogen dissociation degree under the addition of oxygen into the discharge seems to be satisfactory nowadays, there is some experimental evidence that a similar situation may take place even when the admixture is added after the discharge, i.e. into the afterglow [17]. The aim of this study is to contribute to characterizing and understanding this phenomenon. For
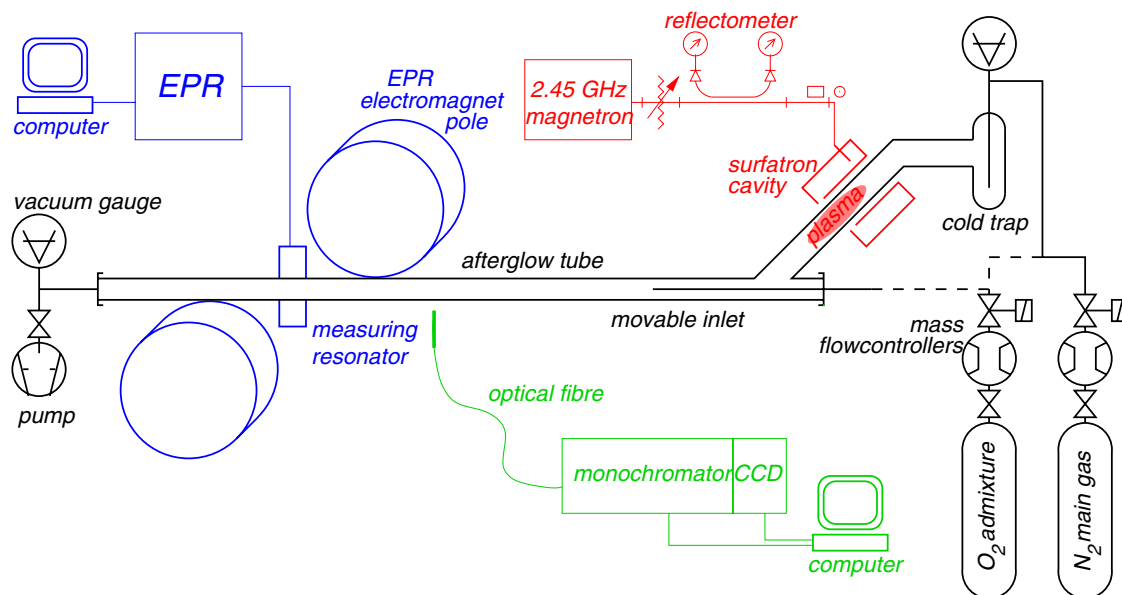
Figure 1. The experimental set-up.

this purpose, herein we present the new measurements of the concentration of N atoms in the afterglow, and investigate how it changes by adding an oxygen admixture either upstream or downstream from the active discharge. As the above-cited hypotheses explaining the dissociation increase were developed primarily for the active discharge, we test their suitability for the description of the kinetic processes taking place in the afterglow.

The experimental set-up and the working conditions of this work are described in the next section. The results are presented in the subsequent section, together with their analysis and discussion. A final section with concluding remarks closes the paper. Our measurements not only give the new results concerning the heavy particle kinetics in the afterglow but also provide a better insight into some still open questions concerning the processes in the N_2–O_2 active discharge, pointing out some possible directions for a future research.

2. Experimental set-up

The experimental set-up shown in figure 1 has been developed in order to add the oxygen into the main gas (nitrogen) either upstream or downstream from the discharge. A microwave discharge was produced in a quartz tube with an inner diameter of 13 mm by a 2.45 GHz microwave generator with 100 W output. Under these conditions the discharge length was approximately 2 cm. The flowing afterglow was observed in a 1 m long quartz tube with an inner diameter of 8 mm. A movable capillary inserted into the afterglow was used for adding oxygen downstream from the discharge. Our experiments were carried out at nitrogen flows of 50 and 100 sccm and pressures ranging from 200 to 1100 Pa. The pressure was set independently from the gas flow by throttling the pump. In order to ensure the purity of the nitrogen gas we eliminated the impurities by a LN_2 cold trap.

The afterglow tube was passing through the measuring resonator of the electron paramagnetic resonance (EPR) JEOL JES-3B spectrometer operating in X-band. The EPR technique was used to measure the concentration of paramagnetic N and O atoms in the ground state. In the EPR spectrometer the atoms and molecules are subjected to a homogeneous magnetic field with an intensity in the order of 10^{-1} T. Due to the Zeeman effect the degenerate energy levels are split into several sublevels. Between them, the magnetic dipole transitions are permitted and so the absorption and the emission of photons are possible. As the energy separation is proportional to the magnetic field, by varying the current passing through the electromagnet there can be found a resonance with fixed frequency impinging microwave beam (wavelength 3 cm). In this resonance, a small part of the microwave beam is absorbed by transitions to the upper state. The integral of the absorption line is proportional to the concentration of paramagnetic particles. In such a manner a slow sweep of the magnetic field is used to record the EPR absorption spectrum. Each paramagnetic atom or molecule has a typical spectrum, given by its electron configuration, and can thus be identified. The overview of the EPR method can be found in [18] and the details concerning its use in gases and plasmas are, for example, in [19, 20]. After the calibration by molecular oxygen [21], which is also paramagnetic, this technique gave the absolute concentration of the measured species. Since the discharge and the afterglow tubes were fixed on a movable support, there was a possibility to vary the distance between the discharge, the admixture inlet and the measuring EPR resonator.

As a complementary method we used the optical emission spectroscopy to record the intensities of the main spectral bands, mainly the 1st positive system of N_2, i.e. transition $N_2(B\,^3\Pi_g) \rightarrow N_2(A\,^3\Sigma_u^+)$ and the β-system of the NO molecule. The spectrometer used was a Jobin-Yvon Triax 320 with 32 cm focal length, 1200 gr mm^{-1} grating and Peltier element cooled CCD camera.

3. Results and discussion

Several investigators have observed an increase in the N atom concentration in the discharge and in the afterglow when O_2 was added into the active N_2 discharge operating at pressures of about 100–1000 Pa [12–14]. Note that when no admixture is added, the N atom density is usually very low (typically ~0.1%). For instance, in [22] the authors stated that using an extra pure nitrogen gas they could not even detect the N atoms in the post-discharge. Consequently, the degree of purity of the gas can be very significant. That being so, the unknown purity of the nitrogen gas in different experiments makes a direct comparison between the results of various research groups rather difficult.

　　As we will see in this work, a definitive explanation of the observed N atom density increase with O_2 admixture is still missing, despite the efforts of many researchers. Besides the experimental difficulties associated with the nitrogen purity, the N_2–O_2 kinetics itself is also quite complex and subject to some uncertainties, which makes the modelling approach a challenge.

　　In order to simplify the analysis, herein we decided to focus our investigation on the addition of the admixture after the active discharge. Considering a mean free path and the gas velocity, it is practically impossible for O_2 molecules to reach the discharge which is 16 cm upstream. Despite this, we verified that the discharge was oxygen free by unsuccessfully trying to find NO_γ optical emissions in the discharge. In this case, the problem reduces to the influence of the kinetics of O_2 added into the N_2 afterglow. The conditions in the discharge are thus constant and independent of the admixture.

　　In spite of our accent on the addition of oxygen in the afterglow, the design of our experimental apparatus (see figure 1) allows adding the oxygen either upstream (into the active discharge) or downstream (into the post-discharge), providing a more complete characterization of the system. The experimental results for both cases are presented in figure 2, where the N atom density is plotted as a function of O_2 admixture. Note that when the admixture is added into the discharge, the results exhibit a similar character to those previously reported [12–14]. We observed, however, a comparable, albeit lower, increase even when the admixture was added into the afterglow itself.

　　In both cases, at a low amount of the oxygen admixture the N atom concentration increases. When O_2 is added into the discharge itself the effect is more pronounced, as the maximal increase is ten fold. For the oxygen added into the afterglow, the maximum value of N is about three times higher than what was measured in pure N_2. Furthermore, the amount of the admixture, which produces the maximum nitrogen dissociation is different in both situations. On the one hand, when the oxygen is added into the discharge, the maximum is reached around 1% of the admixture and then N atom density decreases. On the other hand, when oxygen is added into the afterglow, the maximum appears earlier, at 0.2% of the oxygen content and after that the N atom density is constant.

　　As the EPR technique is based on resonant absorption of microwave radiation on extremely close energy levels (which
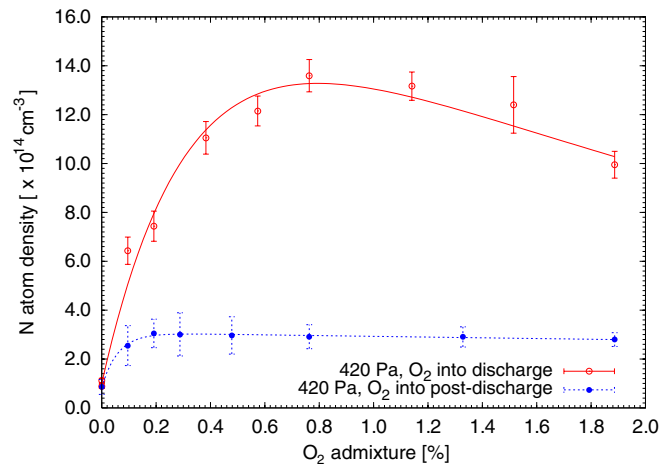

Figure 2. The concentration of N atoms as a function of the oxygen admixture for the pressure 420 Pa. The oxygen is added either upstream or 16 cm downstream from the active discharge. The measurements were carried out in the position 40 cm from the discharge. The nitrogen flow rate was 50 sccm.

have consequently in a thermodynamic equilibrium nearly identical populations) there is always a risk of the absorption saturation. As there is a remote possibility [23] that the presence of the admixture can contribute to the depopulation of the upper level, and by such means virtually increase the observed absorption, we decided to verify the existence of the observed phenomenon by another method.

　　It is a well accepted [12, 24, 25] practice to record the spectral range 570–590 nm in the 1st positive system of N_2. As the recombination of N atoms produces preferably $N_2(B, v = 11)$ states, in the presence of N atoms the vibrational transitions 12–8, 11–7 and 10–6 are amplified. In afterglow conditions, the intensity of these bands is proportional to the square of N atom density. In figure 3 we present the spectrum of N atom recombination radiation for both configurations: the admixture into the discharge and the admixture into the afterglow. As a reference, the spectrum recorded with no admixture is presented, too. A reliable quantitative calculation of the N atom density from the recombination spectra cannot be carried out due to the strong overlapping with the 1st positive system originating from the discharge. However, the increase in the recombination radiation (i.e. the increase in the N atom density) is visible and qualitatively agrees with the absolute data given by the EPR technique.

　　The phenomenon of the N atom density increase with O_2 admixture was observed for several pressures, as depicted in figure 4. This figure shows that the percentage of oxygen that maximizes the concentration of the nitrogen atoms does not depend on the pressure within the range considered in this paper. The only difference is the value of the maximal N concentration, where the highest value is observed at a pressure of 700 Pa.

　　From figures 2–4 it is clearly visible that the effect of the dissociation increase takes place even for O_2 addition outside of the active discharge. In order to try to understand this behaviour, we have to look both at possible additional sources producing N atoms and at a possible diminution of the loss
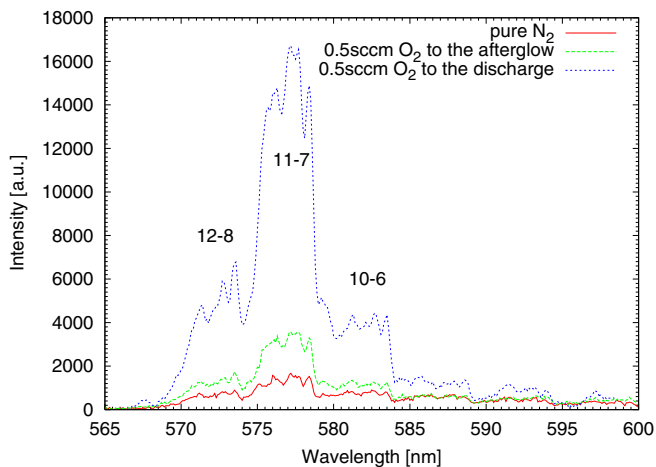
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Figure 3. The portion of the nitrogen 1st positive system spectrum taken in the afterglow (65 cm from the active discharge). The increased intensities of 12–8, 11–7 and 10–6 vibrational transitions are caused by the nitrogen atom recombination. Experimental conditions: pressure 700 Pa, 50 sccm nitrogen flow, oxygen added either into active discharge or 16 cm downstream.
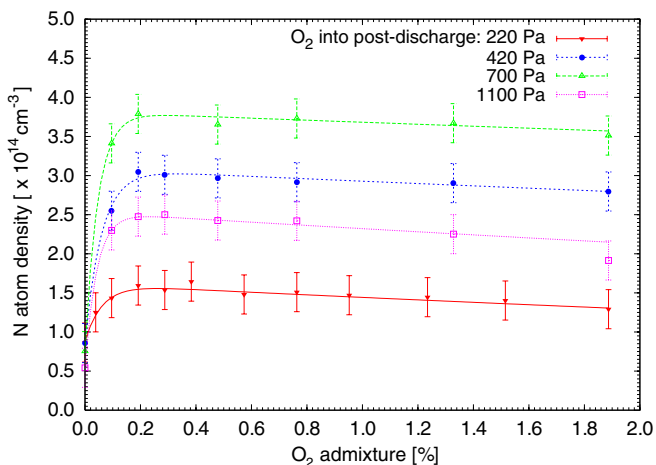

Figure 4. Increase in the nitrogen dissociation due to the oxygen added into the afterglow for several operating pressures. The oxygen is added 16 cm downstream from the active discharge. The measurements were carried out in the position 40 cm from the discharge. The nitrogen flow rate was maintained at 50 sccm while the pump was throttled.

of existing atoms. As will be detailed below, any process responsible for a higher atom production must be of a chemical origin, such as the processes involving vibrational excited states of N_2 [3], since the energy needed for the N_2 dissociation in the afterglow cannot be provided by the electrons. This behaviour would require some energy to be transported from the discharge to the afterglow in the form of energetic particles. On the other hand, a typical example of the loss inhibiting is the poisoning of the wall recombination sites by an admixture, which does not require any additional energy.

If we assume that the observed increase in N atom density when small amounts of O_2 are added into the afterglow is of the same origin as that of the increase when O_2 is added into the discharge, we must discuss the viability of three

generally accepted explanations, namely, (i) the increase in the reduced electric field E/N, (ii) the modification of the surface recombination coefficient and (iii) the importance of homogeneous reactions.

3.1. Increase in E/N in the discharge

In [12] it was shown that the addition of a small percentage of O_2 leads to the decrease in the associative ionization process due to the quenching of the involved excited states and, subsequently, the reduced electric field must increase in order to sustain the discharge. The higher E/N then leads to a larger N atom production via direct electron impact dissociation. This explanation justifies to a large extent the behaviour of N atom density when O_2 is added into the discharge. However, it clearly cannot account for the observed increase in the atomic concentration when the admixture is added into the afterglow. Indeed, there is at most a residual electric field in the afterglow, where the electron impact dissociation is always negligible. Moreover, the electric field in the discharge is not changed by the O_2 addition to the afterglow, so that the amount of N atoms created in the discharge by electron impact is exactly the same.

3.2. Change in surface recombination coefficient

A low pressure dc discharge was studied in [26], where it was shown that for high O_2 percentages (more than several per cent) the modelling and the experimental results agree quite well. However, some discrepancies exist for the lower O_2 admixtures, in particular, in what concerns the increase in N atom density under the addition of O_2. This fact led the authors in [26] to the conclusion that there is a certain range of O_2 percentages where the wall recombination coefficient for N atom decreases with increasing admixture. In such a case, the decrease in the N atom density along the afterglow tube would be more pronounced for the pure nitrogen than in the case of a small amount of an additional O_2 admixture. Inhibiting the wall processes which take place between the O_2 capillary inlet and the point of the measurement would lead to the increased N atom density at the point of the measurement, compared with the N atom density value which was taken in the pure nitrogen case. However, in any case, inhibiting the wall processes cannot lead to an increase in N atom density along the afterglow tube.

To test the validity of this wall effect hypothesis for the admixture added into the afterglow, we measured the N atom density along the afterglow tube with and without the O_2 admixture. The results are shown in figure 5. We observe that without O_2 the N atom density is rather constant, whereas when O_2 is added into the afterglow, the N atom density steeply rises. As we discussed in previous paragraph such behaviour cannot be explained by some inhibition of the loss processes. Therefore, the observed increase in the N atom density along the afterglow tube indicates the presence of N atom producing processes involving oxygen.

The dimensions of the measuring resonator limit the temporal resolution of our apparatus to several milliseconds. The observed increase in N atom density even before the
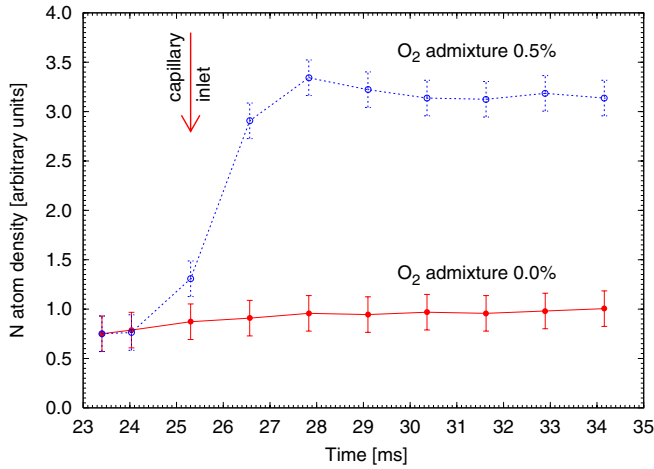
Figure 5. Temporal development of N atoms along the afterglow tube in proximity of the oxygen inlet for zero oxygen flow and 0.5% oxygen admixture. The pressure was 420 Pa, the gas velocity $v = 8\,\mathrm{m\,s^{-1}}$.

Figure 6. The results of model, calculated for the same conditions as are experimental results in figure 4.

capillary inlet can therefore be attributed to a convolution artefact rather than to a backstreaming of admixture. The observed increase is rather fast as it takes place during several milliseconds. Taking into account the temporal resolution, the real increase is probably even faster. Note that a comparable time is needed for the gas mixing itself. The dissociation increase due to the oxygen admixture in the post-discharge therefore has to be caused by fast reactions of the admixture with the energetic species carried by the gas.

3.3. Homogeneous reactions

With the purpose of studying the effect of homogeneous reactions we used a detailed modelling of the kinetic processes that take place in the gas phase. The model developed in [27] has been adapted to account for the oxygen admixture in the afterglow. Hence, the discharge region is described here by the self-consistent determination of the active species concentrations for pure N_2, considering the Boltzmann equation for the electrons coupled to a set of steady-state rate balance equations for the heavy particles produced in the discharge, namely: the vibrational manifold of ground-state nitrogen and oxygen molecules—$N_2(X\,^1\Sigma_g^+,\ v)$ and $O_2(X\,^3\Sigma_g^-,\ v')$ (with $0 \leqslant v \leqslant 45$ and $0 \leqslant v' \leqslant 15$); ground state atoms—$N(^4S)$ and $O(^3P)$; electronic states of molecular and atomic nitrogen and oxygen—$N_2(A\,^3\Sigma_u^+,\ B\,^3\Pi_g,\ B'\,^3\Sigma_u^-,\ C\,^3\Pi_u,\ a'\,^1\Sigma_u^-,\ a\,^1\Pi_g,\ w\,^1\Delta_u)$, $O_2(a\,^1\Delta_g, b\,^1\Sigma_g^+)$ and $N(^2D,\,^2P)$; the radicals—$NO(X\,^2\Pi)$, $NO(A\,^2\Sigma^+)$, $NO(B\,^2\Pi)$, $NO_2(X,\ A)$ and O_3; the main positive ions—$N_2^+(X\,^2\Sigma^+,\ B\,^2\Sigma^+)$, N_4^+, O_2^+, O^+ and NO^+, and negative ions O^-.

Once the concentrations of the various neutral and ionic species are obtained, the relaxation of the most populated heavy species is studied in the afterglow by considering a system of coupled time-varying kinetic master equations, in which the electron impact processes are neglected. This temporal analysis is made in two steps: first we calculate the
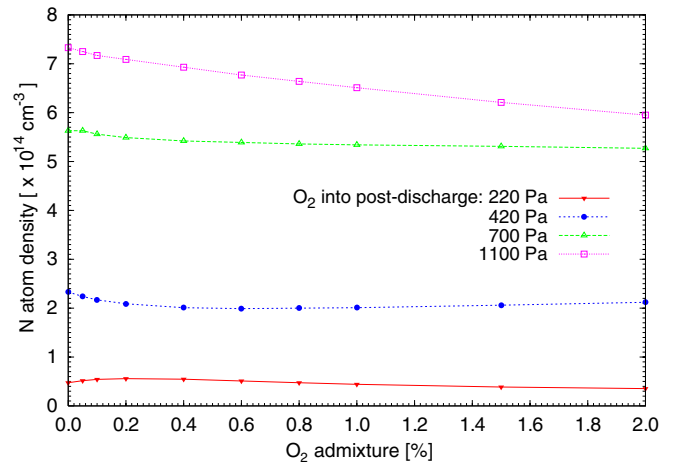
heavy species concentrations in the near afterglow in pure N_2; then, we consider the introduction of a small oxygen percentage into the post-discharge at different distances downstream from the end of the discharge depending on the gas flow rate.

Note that the rate balance equations for the creation and destruction of the different heavy particles take into account the relevant heterogeneous reactions. On the one hand, recombination of atoms on the wall is treated as a first-order process, with a wall recombination probability γ; on the other hand, diffusion of metastable states $N_2(A,\ a',\ a,\ w)$ to the wall is assumed to destroy these states with probability one, whereas $O_2(a, b)$ are destroyed with probabilities $\gamma_a = 10^{-5}$ and $\gamma_b = 2 \times 10^{-2}$ [9]. However, at least one of the nitrogen metastables may have a lower deactivation probability at the wall, as a non-identified slowly diffusing nitrogen metastable state has been reported in [28]. The model predictions have been validated in different discharge and post-discharge conditions [3, 10, 11, 27], but this state may be involved in the explanation of the present measurements, which is still missing for the time being, as discussed below.

The model calculates radially averaged densities, and possible effects of radial profiles are not included directly. Nevertheless, using a 2D model would constitute an interesting refinement, but would hardly bring new physical insight [29]. The atomic nitrogen radial distribution is very flat, due to the low value of the atomic recombination probability in the afterglow. Furthermore, the recombination probabilities are effective first-order recombination probabilities, and by modifying their values one may indirectly include second order effects and/or changes in the atomic flux towards the wall due to radial profiles.

Figure 4 shows the measured and figure 6 the calculated N atoms concentration as a function of the oxygen admixture for a range of pressures. We can see that our calculations fail to fully describe the measured results. As a matter of fact, in spite of the agreement on the order of magnitude of the population of the nitrogen atoms coming from the discharge, their increase with O_2 in the post-discharge is not predicted by the model.

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The numerical calculations indicate that the main processes for N(^{4}S) production in a N$_2$–O$_2$ mixture in the experimental conditions of this work are the following ones: N$_2(X, v \geqslant 12)$ + O $\rightarrow$ NO + N, N$_2(A)$ + NO $\rightarrow$ N$_2(X)$ + N + O and N$_2(a')$ + NO $\rightarrow$ N$_2(X)$ + N + O. However, modelling also shows that the reverse process NO + N $\rightarrow$ N$_2(X, v \simeq 3)$ + O plays a dominant role in the destruction of nitrogen atoms. Hence, NO species contributes not only for N atom production, but also for its destruction. Consequently, our calculations show that the concentration of nitrogen atoms remains practically unchanged with O$_2$ addition in the pressure range considered here.

With respect to other important active species produced in nitrogen–oxygen mixtures, such as oxygen atoms, it is worth noting here that we did not observe it either directly by means of the EPR technique or indirectly by measuring the NO$_\beta$ system near the O$_2$ inlet. Owing to the fact that the detection limit for O atoms in our experiment is of the order $\sim 10^{13}$ cm^{-3}, the oxygen is weakly dissociated. Therefore, the process N$_2(X, v \geqslant 12)$ + O $\rightarrow$ NO + N should not be important, which is in contradiction to our numerical calculations. For this reason, further research should be carried out in order to study to what extent these discrepancies result from some kinetics that was not taken into account in the discharge or in the post-discharge model that could be important under our experimental conditions.

The present experimental results and consequent discussion has shown that the processes responsible for the increase in N atom density when O$_2$ is added into the afterglow cannot be fully described by any of the available explanations developed for the active discharge. Moreover, this also means that even when adding the oxygen into the discharge the three hypotheses are not complete because at least part of the increase in N atom density may be caused by the same unknown processes responsible for the effect in the afterglow.

4. Conclusion

We observed a pronounced increase in the nitrogen dissociation when a small amount of oxygen was added into the pure nitrogen afterglow at pressures in the range 220–1100 Pa. This effect was most pronounced at 700 Pa, where the N atom density reached a value 5 times higher than the one without the oxygen admixture. In comparison with the well-documented influence of the oxygen admixture added upstream of the active discharge, the observed increase is several times lower. Time resolved measurements were carried out and have shown that the increase in N atom density is very fast, taking place during a few milliseconds.

We have shown that none of the different mechanisms previously proposed in the literature, which are relevant for the active discharge, can explain the observed increase in N atom density when O$_2$ is added into the afterglow. The behaviour of N atom density in the proximity of the oxygen inlet proves that the higher nitrogen dissociation is caused by the production of N atoms in the afterglow and not by the inhibition of some loss process. As a certain amount of energy is needed for the dissociation, the production must be caused by some

long-lived energy carrying species, such as N$_2$ metastables or vibrationally excited states. In the study of the nitrogen pink afterglow, these species were shown to have the ability to store energy for relatively long times and transfer it later during the afterglow [2, 3]. However, in the present case it is still not clear which mechanism could justify the observed increase in the nitrogen dissociation degree.

The actual plasma chemical processes responsible for the increase in the nitrogen dissociation degree still remain unidentified and a further experimental and theoretical investigation is needed to clarify this issue. Once the new mechanisms are discovered, their possible influence on the active discharge should be studied and tested by including them in the corresponding models.

Acknowledgments

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