INCREASE OF DISSOCIATION DEGREE IN AFTERGLOW DUE TO ADMIXTURES *

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When a small amount of impurity (O_2, H_2, Ar, Ne, ...) is added to a molecular gas, one observes increased dissociation in the discharge afterglow. In this work we compare two cases: when admixtures are added upstream or downstream of the discharge. Concentration of atoms was measured by means of electron paramgnetic resonance (EPR).

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1 Introduction

One can observe growing interest in non-equilibrium kinetics of low pressure plasmas in nitrogen, oxygen and their mixtures. It is caused by the needs of various branches of science, e.g. physics of the upper atmosphere or plasma physics and technology (cleaning of pollutants, plasma processing).

In many studies various authors observed that even a small admixture to a main gas changes radically the production of atoms (for extensive list see [1]). It is generally supposed that surface reactions, influencing recombination rate, play a dominant role in this phenomenon [2]. Surface reactions in discharge tube are more important than those in afterglow due to strong bombardment of discharge tube walls. Therefore we compare the results when admixture is added upstream or downstream from the discharge.

In this work we concentrate on O_2, Ne and NO admixtures. Nitric oxide is often used in diagnostics of nitrogen discharges for chemical titration of nitrogen atoms. Therefore the question if such titration changes the processes in afterglow or not, is of great importance.

2 Experimental setup

A microwave discharge is produced in a quartz discharge tube with inner diameter of 13 mm by means of surfatron cavity, powered by 100 W magnetron working at 2.45 GHz. Our experiments being carried out in a flowing regime, afterglow is observed downstream in 1 m long quartz tube with inner diameter of 8 mm. Small amount of admixture may be added either to a main gas before its passing through the discharge, either through a capillary directly into afterglow.

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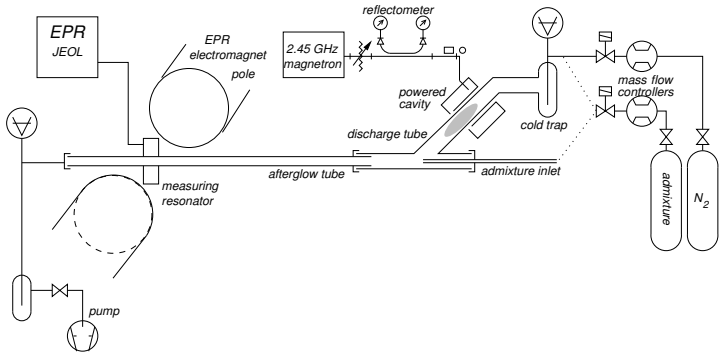

Fig. 1. Schematic drawing of experimental apparatus.

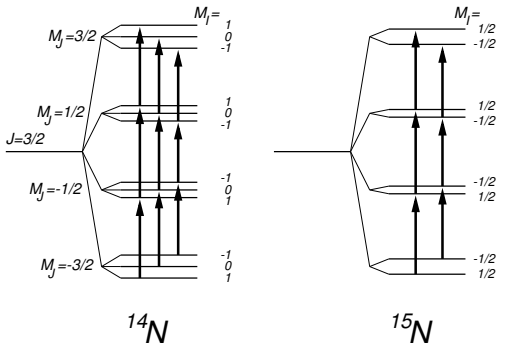

Fig. 2. Transitions between Zeeman split energy levels in microwave region.

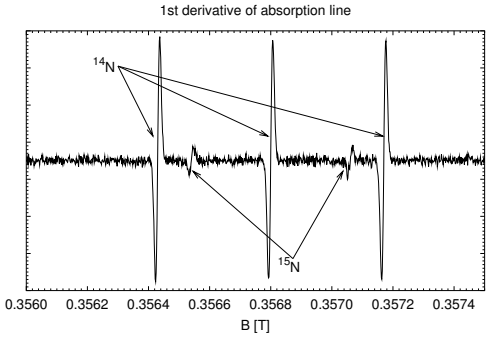

Fig. 3. Typical EPR spectrum of nitrogen atoms.

The gases are led from gas bottles through the mass flow controllers to a cold trap, which removes traces of unwanted impurities, like a water or hydrocarbons. The purities of all used gases were better than 99.995% according to manufacturers' certificates. Flow rate of admixture was varied between 0 and $1.6{\cdot}10^{-2}$ Pa·m^3·s^{-1}, nitrogen flow rate being kept constant at $1.6{\cdot}10^{-1}$ Pa·m^3·s^{-1}. The pressure in the discharge was 380 Pa. Total desorption and leak rate was around 10^{-6} Pa·m^3·s^{-1} after thorough degassing.

3 EPR spectroscopy

We employed electron paramagnetic resonance spectrometer JEOL JES-3B operating in X-band to measure the concentration of atomic nitrogen. This method is based on resonance absorption of microwave energy by the transitions between Zeeman split levels. In the case of nitrogen, the ground level $^4S_{3/2}$ have non-zero magnetic momentum, and thus it is used most often. Due to a nuclear spin I=1 of ^{14}N, resulting EPR spectra have typical triplet structure. After a calibration of the EPR device by molecular oxygen [3], which is paramagnetic, the absolute concentration

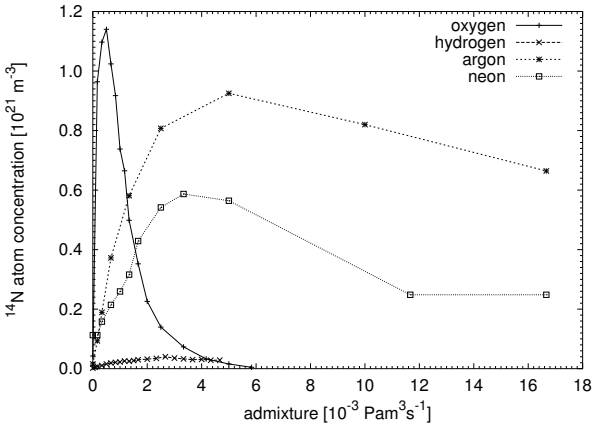

Fig. 4. Influence of various admixtures added upstream (before discharge) to nitrogen gas on N atom concentration in afterglow. Nitrogen flow was $0.8{\cdot}10^{-1}$ Pa·m^3·s^{-1} and corresponding pressure was 450 Pa.

was obtained. The advantage of such calibration is well defined fill factor, which is not easy to achieve with traditional DPPH (diphenylpicrylhydrazine) standard. In comparison with other techniques it has a big advantage in its non-invasivity and the ability to determine the absolute concentrations of wide range of species [4].

4 Results and discussion

Addition of small amount of oxygen impurity into nitrogen gas prior to its passage through the discharge may give raise to more than ten-fold increase in N atom concentration in the afterglow. This effect was observed also for other main gases (N_2, O_2, H_2) and admixtures (N_2, O_2, H_2, Ar, Ne). Taking into account the most common reactions in above mentioned mixtures (e.g. [5]) and our experimental conditions, the observed behaviour can not be explained solely by volume reactions. Thus it is generally attributed to the changes in surface kinetics, where active sites [6] are occupied by admixture atoms and thus recombination of atomic nitrogen is less probable [7].

Bombardment by ions, electrons and other species in the discharge contributes to the 'activation' of the quartz surface, i.e. the number of active sites increases [8]. Therefore the surface reactions on walls exposed to the discharge are more important than those occurring on the walls exposed only to afterglow.

Figures 4 and 5 show the results when admixtures are added upstream or downstream of the discharge. It is clear that increase in dissociation rate is much bigger when admixtures pass through the discharge.

Very interesting behaviour is observed for NO admixture. After the maximum a steep decrease follows. It is caused by fast reaction

$$\mathrm{N} + \mathrm{NO} \rightarrow \mathrm{N_2} + \mathrm{O}$$

which is important for above mentioned titration. We can see that N atoms vanish for NO flow around $2.1{\cdot}10^{-3}$ Pa·m^3·s^{-1}, which corresponds to N concentration $1.1{\cdot}10^{21}$m^{-3}. The initial N

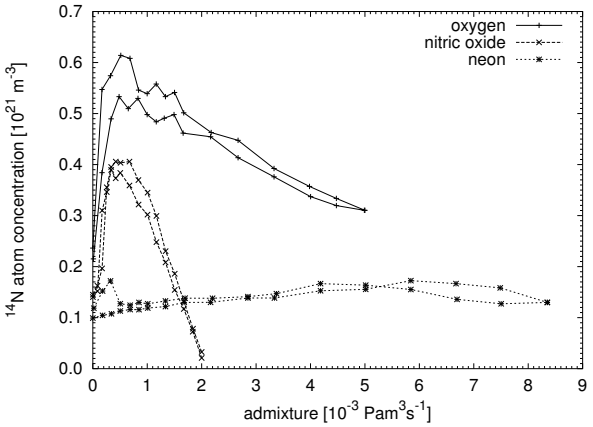

Fig. 5. Influence of various admixtures added downstream (into the afterglow) to nitrogen gas on N atom concentration in afterglow. Nitrogen flow was $1.6{\cdot}10^{-1}$ Pa·m^3·s^{-1} and corresponding pressure was 380 Pa.

density measured directly by EPR is $1.4{\cdot}10^{21}$m^{-3}. So both values correspond very well. But between them the N concentration actually rises, which is unexpected.

5 Conclusion

Impurities added in relatively small quantities to the nitrogen gas enhance the production of nitrogen atoms. Increase in dissociation rate is greater when admixture is added upstream from discharge. As surface reactions are responsible for this increase, walls exposed to discharge have higher reactivity that walls in the afterglow.

Nitric oxide is often used for diagnostic purposes in nitrogen plasmas. Our measurement show that influence of NO admixture in afterglow is much more complex than simple titration reaction. We observe important increase in N atom concentration during titration, but it seems that its results are correct.

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