Measurement of concentration of N atoms in afterglow

V. Kudrle, P. Vašina, A. Tálský, J. Janča

Department of Physical Electronics, Masaryk University,
Kotlářská 2, CZ-61137 Brno, Czech Republic

In this paper we compare different methods for determination of nitrogen atom concentration in afterglow. We employed titration by nitric oxide, electron paramagnetic resonance and optical emission spectroscopy. When correctly carried out, all methods give the same result within experimental error margin. However certain discrepancy exists when small amount of admixture is present.

1 Introduction

As nitrogen containing plasmas are commonly used both in research and technology, the concentration of nitrogen atoms in discharge afterglow is often sought. To obtain relative concentrations one may apply various experimental techniques, but only few of them are suitable for absolute measurements. Widely accepted method[1] is a gas phase titration by nitric oxide (NO).

However it is well known, that even a small amount of admixture can increase a dissociation degree in afterglow. It is generally accepted [2] that surface processes play a dominant role in this effect. Particularly important are the changes of surface recombination rate, which in turn directly influences the density of atoms. Such effect we observed [3, 4] for many combinations of main gas and admixture (N_2, O_2, Ar, Ne, H_2, ...). When admixture is added into the discharge, dissociation degree may be more than one order higher than for pure molecular gas. When the admixture is added to afterglow, the rise is lower but it is still quite important.

Therefore validity of titration (and other techniques, like actinometry) may be questioned, if presence of NO in the afterglow changes e.g. surface recombination rate of atomic nitrogen. In this work we compare and discuss the results of NO titration and those obtained from EPR spectroscopy, which gives absolute value of concentration of nitrogen atoms in ground state.

2 Experimental setup

Schematic drawing of the experimental apparatus is presented in Fig. 1. An electrodeless capacitively coupled RF discharge (13.56 MHz, 75 W) was produced in the quartz tube with inner diameter of 37 mm. The flow of working gas, nitrogen, was held at 200 sccm by mass flow–controller. Corresponding pressure was 590 Pa. In the discharge the nitrogen was partially dissociated and passed through the right–angle to an afterglow region with X–band EPR spectrometer on its end.

Small amount of NO (several sccm) was injected between the discharge and the EPR resonator by means of capillary with diffuser. Optical emission from the afterglow was recorded from the region behind several bends to prevent direct observation of discharge area. Optical fibre was connected to monochromator (Jobin–Yvon TRIAX 320) equipped with CCD camera.
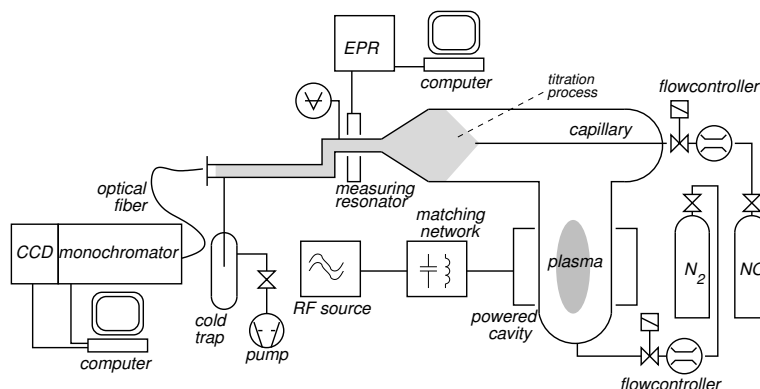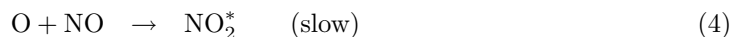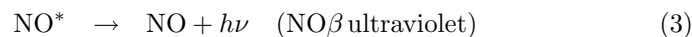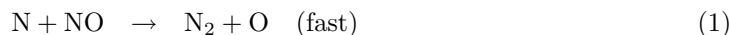

Fig. 1. Schematic drawing of experimental apparatus.

We employed electron paramagnetic resonance (EPR) spectrometer Zeiss ER–9 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 [5]. After a calibration of the EPR device by molecular oxygen [6], which is paramagnetic, the absolute concentration was obtained. The advantage of such calibration is well defined fill factor, which is not easy to achieve with traditional DPPH 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.

3 Results and discussion

When nitric oxide is added to nitrogen afterglow, several reactions take place:

$$N + NO \quad \rightarrow \quad N_2 + O \quad \text{(fast)} \tag{1}$$
$$O + N + M \quad \rightarrow \quad NO^* + M \quad \text{(slow)} \tag{2}$$
$$NO^* \quad \rightarrow \quad NO + h\nu \quad (NO\beta \,\text{ultraviolet}) \tag{3}$$
$$O + NO \quad \rightarrow \quad NO_2^* \quad \text{(slow)} \tag{4}$$
$$NO_2^* \quad \rightarrow \quad NO_2 + h\nu \quad \text{(green} - -\text{yellow)} \tag{5}$$

If there is less NO than N, all NO molecules are consumed by reaction (1) and by reactions (2), (3) strong NOβ emission in UV is produced. If NO is more abundant than N, reactions (4), (5) take place and one may observe green–yellow continuum of NO_2. When concentrations of N and NO are the same, no emission is observed (dark point).

Unfortunately, many authors do not take into account that reactions are relatively slow and thus sufficient reaction time must be given. When this condition is not satisfied, the dark point is very badly defined. This is shown in Fig. 2, where the solution of kinetic equations (1)–(5) is presented. Corresponding experimental results for two distances between NO inlet and optical fibre are shown in Fig. 3.
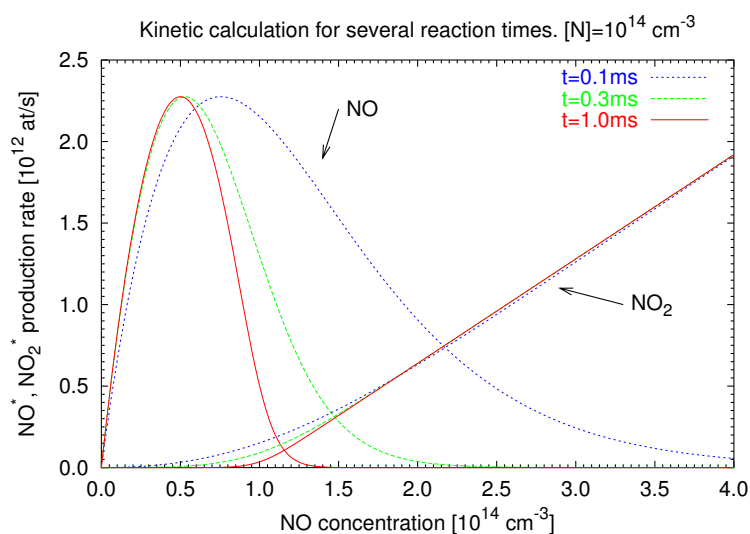

Fig. 2. Optical emissions calculated from equations (1)–(5) for three reaction times. Rate coefficients are taken from [1].

Now the question arises whether the presence even of a small NO admixture can change also other processes in afterglow. Similar phenomenon was observed for many combinations of working gas and admixture [3]. The results for air admixture are presented in Fig. 4. The concentration of atomic nitrogen increases nearly two times, when air is added to the afterglow. This can be explained by heterogeneous reactions, where the surface recombination coefficient of N is affected by physi– and chemisorbed molecules of admixture[4].

To see whether NO besides reactions (1)–(5) has also other effects (such as above mentioned heterogeneous reactions), we measured both EPR intensities and OES intensities during NO titration process. As amount of NO titrant is increased, due to reaction (1) concentration of N should decrease linearly. This can be detected by EPR spectrometer. Also the intensities of 12–8, 11–7, 10–6 vibrational bands
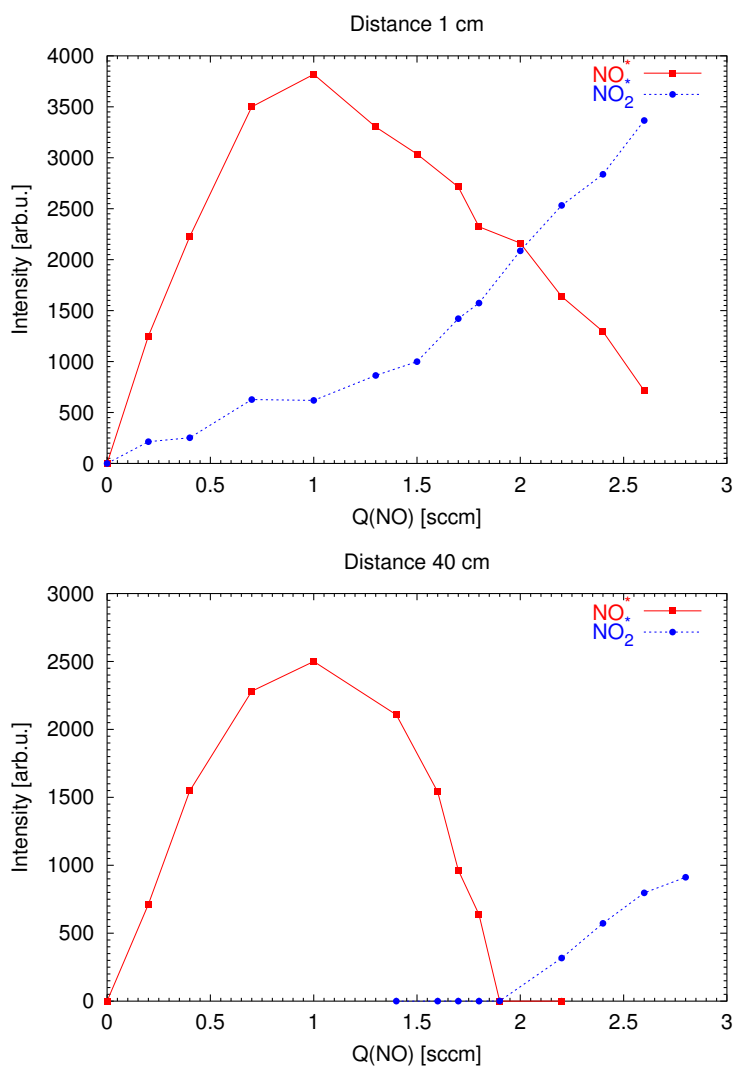
Distance 1 cm

Distance 40 cm

Fig. 3. Experimental results of titration. Dark point is well defined only for sufficiently long reaction time (bottom figure).

of first positive system $(B^3\Pi_g \to A^3\Sigma_u^+)$ of nitrogen decrease, because vibrational levels v=10,11,12 are mainly populated by N atoms recombination. As the intensity is proportional to square of N atom density, square root of these bands intensity linearly decreases with NO amount.

We can see, that position of a dark point from Fig. 3 corresponds very well with the instant (Q_{NO}=1.9 sccm) where all N atoms disappear due to fast reaction (1).
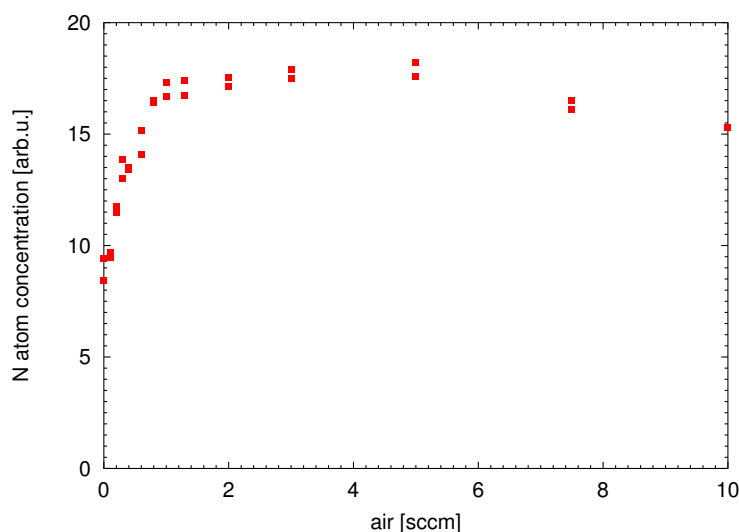
Fig. 4. Influence of air admixture added to the afterglow. N concentration is measured by EPR.

The intensity of N_2 'recombination' band decreases to zero, too. Absolute value of N concentration, determined from dark point is $[N]=1.3\times10^{15}$ cm^{-3}. When EPR is calibrated by molecular oxygen, we get $[N]=1.0\times10^{15}$ cm^{-3}. This is good agreement, when experimental errors (20%) are taken into account. However the shape of EPR signal for low NO concentrations suggest that there is some systematic difference between EPR and titration.

It seems that there are two possibilities: (i) presence of NO in small quantities may give rise to concentration of nitrogen atoms. This can be explained by surface reactions, where the NO molecules occupy active recombination sites. (ii) EPR detects N atoms in ground state only but titration is sensitive also to excited ones. If there is substantial fraction of excited atoms in afterglow and they are deexcited by admixture, this can explain observed data.

4   Conclusions

The results of NO titration, OES and EPR are in good agreement within experimental error margin. To achieve such agreement, careful design of apparatus is necessary, especially sufficient reaction time for NO titration.

However, certain difference between these methods exist, as demonstrated for low NO admixtures. It is not yet clear, whether titration is 'correct' and EPR does not detect excited species or EPR is 'correct' and NO titration increases the N atom concentration due to surface effects. In the latter case this conclusion should
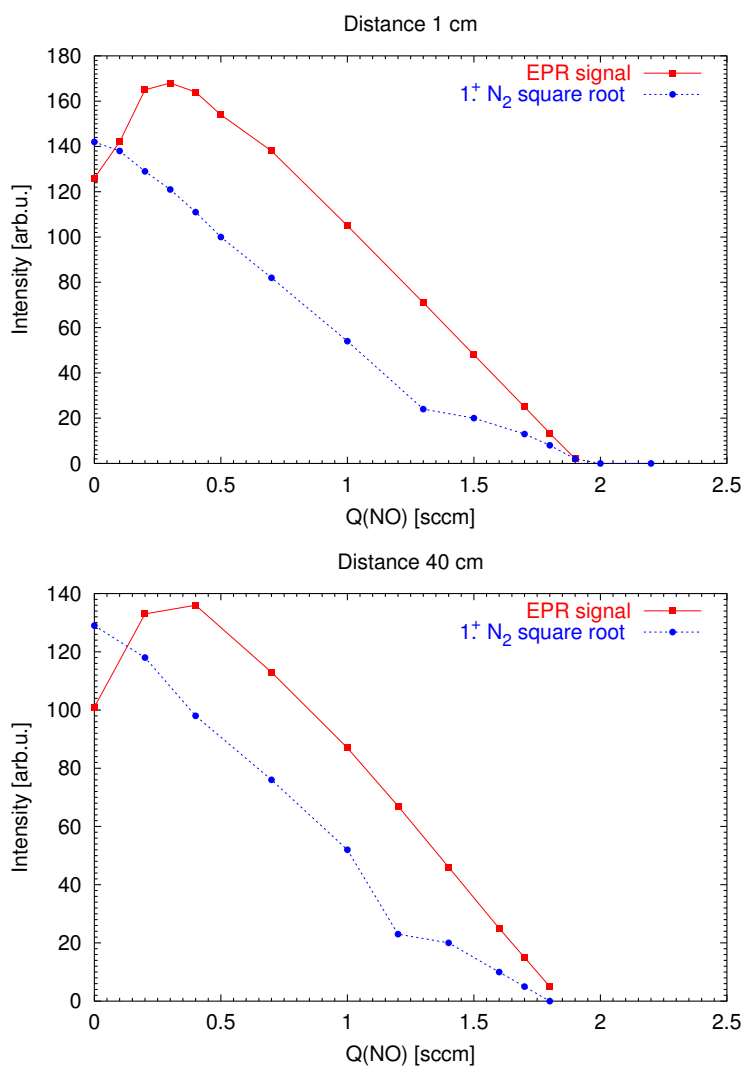
Distance 1 cm

Distance 40 cm

Fig. 5. Comparison of EPR signal and square root of 11–7 vibrational band of first positive system of nitrogen for two distances between the NO inlet and the measuring point.

be taken into account, when employing also other diagnostic techniques, such as actinometry.

References

[1] A. Ricard: *Reactive plasmas*, SFV, Paris, 1996

[2] B. Gordiets *et al*: J.Phys.D: Appl. Phys. **29** (1996) 1021.

[3] V. Kudrle, A. Tálský, J. Janča: *Proceedings of XXIV ICPIG*, Warszava 1999, p. 167.

[4] V. Kudrle, A. Tálský, A. Kudláč, V. Křápek, J. Janča: Czech. J. Phys. **50** (2000) 305.

[5] A. A. Westenberg: Prog. React. Kinet. **7** (1973) 23.

[6] S. Krongelb, H. W. P. Strandberg: J. Chem. Phys. **31** (1959) 1196.