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Absolute production rate measurements of nitric oxide by an atmospheric pressure plasma jet (APPJ)

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Abstract

Tunable diode laser absorption spectroscopy (TDLAS) has been applied to measure the absolute production rate of NO molecules in the gas phase of an atmospheric pressure plasma jet (APPJ) operating at rf (13.56 MHz) in argon with small (up to 1%) admixtures of air. The resulting NO production rates were found to be in the range \((0.1–80 \times 10^{-3})\) sccm or \((0.05–35 \times 10^{18})\) molecules s\(^{-1}\) depending on the experimental conditions. Maximum rates were obtained at 0.2\% air. For TDLAS measurements the APPJ was arranged inside an astigmatic multi-pass cell of Herriott type with 100 m absorption length. The insertion into a closed volume differs slightly from the normal, open operation with the jet propagating freely into air. Therefore, the measuring results are compared with optical emission of the open jet to verify equivalent experimental conditions. The dependence of the optical emission of NO (237 nm) on power and gas mixture has been measured. The similar shape of the dependence of absorption and emission signals gives evidence that the comparability of experimental conditions is sufficiently satisfied. It is concluded that the NO production rate of the APPJ in ambient air can be characterized using TDLAS and provides reliable results in spite of differing experimental conditions due to the set-up.

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

1. Introduction

Atmospheric pressure plasma jets (APPJ) have been established as sources of non-equilibrium, atmospheric pressure plasmas [1–9]. A recent compilation summarizes different physical approaches and technical solutions [10]. The main peculiarity of these sources is that the jet is not confined by electrodes and its dimension can be adjusted in a wide range from several cm down to the sub-mm region thus allowing local treatment of 3D surfaces, e.g. the inner walls of wells, trenches or cavities. Among other applications, the treatment of temperature-sensitive surfaces such as biological material is of interest, in particular the interaction of the plasma with living cells, tissues and bacteria, e.g. for cultivation, deactivation or remedial treatment of diseases.

Here, a non-thermal, rf capillary jet at 13.56 MHz is studied, which is operated with argon and small admixtures (<1\%) of air. The temperature load of substrates remains low, allowing the exposure to fragile surfaces, such as polymers, paper or aforementioned biological matter. The VUV radiation (115–200 nm) of the plasma source has been quantified [2] and the UV spectrum between 200 and 400 nm, measured by optical emission spectroscopy (OES), has been described [3].

Next to the 2nd positive system of N\(_2\) and the 3064 Å system of OH, emissions of nitric oxide (NO, \(\gamma\) System) were detected. In biomedicine, the role of nitric oxide (NO) molecules among other chemically active species is considered essential for living organisms, as it induces specific chemical reactions and thus participates in many physiological processes. In particular, the treatment of cardiovascular diseases is often coupled to application of NO. Therefore, the study of NO production provides a prerequisite for a potential plasma therapy as a future application [5].
Besides OES, production of NO molecules in atmospheric jets has also been found using a mass spectrometer [6]. However, gas extraction and pressure reduction are mandatory to apply mass spectrometry at atmosphere. Moreover, the absolute calibration of the ion signal requires additional effort.

In this work, tunable diode laser absorption spectroscopy (TDLAS) has been applied to measure the absolute production rate of NO molecules. TDLAS allows the direct deduction of ground state densities at absolute scale from measured absorption signals with known spectroscopic constants. This describes a methodological advantage compared with OES, which is restricted to the measurement of electronically excited molecules. A kinetic model is required to deduce the densities of molecules in ground electronic states from the measured densities of excited states.

The NO molecule is characterized by strong absorption bands in the middle infrared part of the spectrum and its spectroscopic properties at room temperature are well known [11]. TDLAS was applied before for measurements of NO in gas discharges [12]. It has been shown in numerous cases that the technique allows the measurement of absolute concentrations of gaseous species present in gas discharges. Most of these discharges were operated under low pressure conditions and their typical dimensions were in the dm range [13]. The aim of this work is to adopt the TDLAS technique specifically to the APPJ in order to demonstrate its capability to provide reliable measurements even under unfavourable conditions present in APPJ, namely its small dimension, short absorption length, jet geometry, high gas flow conditions, etc. Furthermore, the absolute production rate of the NO molecule shall be deduced depending on rf power and percentage of air admixture. Additional OES measurements are performed and the results are put in perspective to those obtained with TDLAS to validate the results with an independent method.

2. Experimental set-up

2.1. Plasma source configuration

The principle of the APPJ is shown schematically in figure 1. The power supply (13.56 MHz) is connected to the centre rod electrode through a matching network with a \( \pi \)-filter. The electrode is surrounded by a ceramic cap (about 1 cm diameter), which forms the gas stream. Optionally, a ring electrode can be attached, which is connected to the ground. The electrode helps to stabilize the operation of the jet. Nevertheless, if the ground electrode is not fitted, a jet is formed, too. In this case, the discharge circuit is closed by the stray capacitors to the surrounding. The rf power coupled into the discharge is not measured directly at the source, the power values reported here correspond to the values displayed at the generator (difference of forward and reflected power). The gas flow varies between 5 and 10 slm argon and 1–100 sccm of compressed air.

The photograph in figure 2 depicts the APPJ propagating in ambient air and with attached ring ground electrode.

2.2. TDLAS arrangement

Absorption measurements were performed with the transportable two laser beam infrared (TOBI) system [14]. The system is equipped with an astigmatic Herriott multi-pass cell (100 m optical path in 3 l volume). A glass cylinder which forms a quasi-closed volume is placed between the two mirrors of the cell. The APPJ was mounted on the glass cylinder with its tip pointing inwards. The arrangement is shown in figures 3 and 4. Build-up of pressure inside the cell during APPJ operation is prevented by a small orifice in the far side of the confinement.

The typical application of the APPJ is its operation in ambient air, with the process gas (rare gas, nitrogen or other reactive gases and their mixtures) propagating freely into the...
surrounding atmosphere. That situation is different from the closed volume of the multi-pass cell, where the discharge has been operated during the TDLAS measurements. Here, the surrounding gas contains a much higher Ar content, increasing the tendency of the discharge to alleviate arcing which would lead to a lesser stability. Therefore, it is necessary to remove the ground electrode during TDLAS measurements. Throughout all TDLAS measurements, the source was operated without ground electrode.

The NO concentration measured by TDLAS corresponds to the average concentration over the measuring volume, i.e. the entire volume of the multi-pass cell. Therefore, the values for the NO production rate are valid under the presumption that NO formed in the plasma is redistributed homogeneously in the multi-pass cell. Furthermore, a possible influence of temperature gradients to the density measurements can be neglected, because of the relatively small volume of the plasma in conjunction with its mild temperature. For a similar plasma source, temperatures in the range between 35 and 95 °C have been obtained [2], substantiating the assumption of a limited temperature influence.

2.3. OES arrangement

The experimental set-up for OES is shown schematically in figure 5. The APPJ was pointed towards the entrance of an UV-transparent optical fibre, which was situated at a distance of approximately 10 cm from the jet. A CCD-Camera (Andor DU 440 BU2) coupled to a 0.5 m monochromator (Acton2500i) served as detector. The identification of the molecular band was performed with a grating of 2400 lines mm\(^{-1}\), while peak intensities have been measured with a grating of 150 lines mm\(^{-1}\). The jet was operated in ambient air with and without grounded ring electrode.

3. Experimental procedure of TDLAS

The infrared laser diode of the TOBI system was operated in pulse mode using the TDL WINTEL software [15]. During the pulse, the laser emission is swept across the transition frequency of the absorption line. At the end of the pulse, the laser diode is switched off by the software. The last sequence of recorded data corresponds to zero level, see figures 6(a) and 7. The simulated and measured spectra of NO and carbonyl sulfide (OCS) in low pressure reference gas cells serve for spectra identification, see figure 6. Wavelength calibration is carried out with a Fabry–Perot interferometer (1 inch Ge etalon). The recorded etalon fringes are also plotted in figure 6.

The measured data are real-time fitted by TDL WINTEL based on spectroscopic constants listed in the HITRAN database [11]. An example fit is shown in figure 7. It is worth noting that due to the fitting procedure information about the molecular density is derived from the measured differential absorption coefficient rather than from the integral absorption coefficient. The experimental error of such procedure is less sensitive to overlapping of the wings or to saturation of the spectroscopic lines but influenced by the precision of the pressure measurement and the determination of the instrumental profile. The instrumental broadening was estimated by measuring spectra of gases in low pressure reference gas cells.

The set-up is purged with 10 slm Ar for about 4 min prior to the experiment to ensure a sufficient substitution of air by Ar in the entire (3 l) volume of the cell. An example illustrates the time dependence of the density measured in the multi-pass cell in figure 8. Without plasma there is no production...
of NO molecules. Here, the fit produces slightly negative values without physical meaning. This can be considered as an indication for the detection limits of the system and is mostly due to noise. A step in the curve is observed after plasma ignition demonstrating a minor NO production even in the Ar discharge. This is caused by the presence of minor air decontaminations either by back diffusion or desorption from the glass wall.

An addition of air to the Ar flow significantly increases the NO production. A stabilization time of approximately 2 min is needed to provide conditions that are sufficiently constant to produce values within the estimated experimental error of 10% due to the uncertainty in the base line determination. A prolonged stabilization time is necessary after switching off the air flow (marker ‘Air flow off’, figure 8). The slow decay is due to the residual amount of air present in the system behind the mass flow meter. This would require a stabilization time of more than 20 min. The situation of switching off the air flow is not of practical relevance for the normal measuring cycle, though. To test for sufficient repeatability, measurements were performed by adjusting the external parameters (power and air admixture) in both directions, increasing and decreasing values to visualize the error due to insufficient stabilization time. Both data sets are in fairly good agreement and are shown in figures 9 and 10.

The ratio of the numbers of NO and the total number of particles is directly measured with the TOBI system. The data points at stationary level (figure 8) are averaged over a period of approximately 1 min and provide the values from which the absolute production rate is derived by multiplication of these values with the total flow.

The spikes in figure 8 are produced by data points whose fit is apparently wrong. This can be due to a change in the refractive index along the optical path caused by the plasma. The effect can be demonstrated with the periodical movement of the spot of a red alignment laser over the mirror surface which is observed during discharge operation. Due to this influence the measured laser intensity is modulated and the fluctuation of the baseline might cause occasional, faulty fit procedures.

4. Absolute production rate

The NO production rate $X$ can be introduced as additional flow rate into the multi-pass cell. Usually, gas flows are measured in units of standard volume per time unit. Changes in the number of NO molecules, $dN_{NO}$, in the cell volume during a time interval $dt$ can be expressed as:

$$dN_{NO} = n_0 X dt - \frac{n_{NO}}{n} n_0 \Phi dt,$$

(1)

where $n_0$ is the concentration of particles in a standard volume, $n$ and $n_{NO}$ are the total particle and NO concentrations in the multi-pass cell and $\Phi$ is the total output flow.

The change in the number of molecules equals zero for stationary conditions and the production rate of the NO molecules can be derived from equation (1) and expressed as:

$$X = \frac{n_{NO}}{n} \Phi.$$  

(2)

Under our experimental conditions, the process gas mixture contains mainly Ar and only a small percentage of (up to 1%) air. Therefore, an increase in the total particle concentration due to dissociation of molecules is negligible.
compared with the total flow and the input and output flows can be assumed to be equal. Equation (2) represents the fact that the ratio of species concentrations is equal to the ratio of input flows.

5. Results and discussion

5.1. NO production rate determined by TDLAS

The production rate of NO as a function of applied power is shown in figure 9. The curve shows a linear increase for applied powers up to 15 W. The measurements were restricted to 20 W due to attaining the upper detection limit of the experimental set-up at production rates of 0.08 sccm. This upper detection limit is related to a strong overlap of the line wings at higher NO concentrations. Moreover, influences of the plasma on the optical path become stronger at higher powers, complicating an accurate determination of the baseline.

The production rate of NO over air admixture is shown in figure 10. The rising NO production with air flow is apparently related to the increasing amount of precursors for the formation of NO. Low concentration of the starting substance favours the production terms, in general. Several reasons can cause the observed decrease at higher air admixtures. One could be the altered discharge characteristics, for example the electron velocity distribution function. Moreover, further oxidation of NO may play a role at higher air admixtures, for example reactions with molecular oxygen to produce NO2.

It becomes obvious that the production rate depends more strongly on the gas composition than on the total flow. A doubling of the total flow from 5 to 10 sLM results only in slightly lower maximum values and a flatter curve. The air admixture is therefore a very sensitive parameter to control the NO production. For the NO production, a maximum value of $3.5 \times 10^{19}$ molecules s$^{-1}$ is obtained at 0.25% air admixture and an applied power of 20 W.

5.2. NO production analysed by OES

It has been mentioned in the former paragraph that the TDLAS measurements are carried out in a set-up that differs partly from normal operation conditions. Thus, it becomes necessary to validate the results with an independent method. Additional OES measurements have been performed and the results are put in perspective to those obtained with TDLAS.

An overview of the UV spectrum emitted with and without grounded electrode is shown in figure 11. The total emission of the APPJ drops drastically after removal of the electrode. Most probably, the removal of the ring electrode is associated with a change in rf power coupled into the plasma. This, however, cannot be observed by monitoring the output of the power supply.

The emission of the molecular band at 237 nm, see figure 11, has been evaluated for quantitative measurements of the NO emission. The peak intensity as a function of rf power measured with and without ring grounded electrode is plotted in figure 12, together with the NO production rate obtained from TDLAS. It is again obvious that the NO intensity is higher when the ring electrode is applied. Furthermore, the minimum power necessary to operate the discharge is lower in relation to the configuration without ring. The reduction in the required minimum power is additional proof that the fraction of power coupled into the plasma is not the same.

It can be derived from figure 12 that the NO production rate measured in an argon enriched atmosphere of the multi-pass cell without ring electrode shows the same relative behaviour as the emission signal measured with ring electrode in ambient air, rather than the emission without ring. In both cases, the minimum rf power required for ignition is about 5 W. Both curves exhibit a similar linear dependence between 8 and 15 W that goes over into a similar non-linearity between 15 and 20 W. The operation without ring electrode in ambient air, on the other hand, needs a higher minimum power of about 10 W and its different relative behaviour becomes apparent after normalization of absorption and emission signals.

We note here that the dissipation of power in the transmission line and matching network is not considered, because the power was determined only as difference in forward and reflected power measured at output of the power supply. Thus, the power coupled into the plasma represents only a fraction of the values given in figures 9 and 12. The observation of a similar relative power dependence of emission...
and absorption signals could be interpreted as an indication that certainly both configurations provide comparable power coupling.

Relative NO emission intensities and NO production curves (from figure 10) as a function of air admixture are plotted in figure 13. The NO intensities were measured with ground electrode present in ambient air and multiplied with their respective Ar flows. The comparison with the corresponding NO production rates reveals that the dependences measured in emission and absorption are correlated. Their shape coincides in relative scale for the range of up to 0.2% air admixture. Therefore, the emission signal multiplied with the Ar flow can be seen as a measure of the relative NO production rate at small air admixtures.

While the power dependence of the NO emission (figure 12) could be measured with both electrode configurations (with and without ground electrode attached) the NO emission at different air admixtures could be obtained only with ground electrode attached due to technical reasons. The discharge in air is less stable without grounded electrode. The changing of the gas composition often extinguishes the discharge and thus complicates to establish a reliable measurement sequence.

The particular fraction of applied power that is coupled into discharge is a crucial parameter for NO production. Besides on the operational parameters of the APPJ, it depends on the mixture of the surrounding gas and electrode configuration, too. The results imply that the applied rf power couples into the discharge more efficiently when the surrounding is enriched with Ar as compared with air. The ground ring electrode can be applied when the APPJ operates in ambient air to compensate the different power coupling efficiency. This assumption needs to be verified with a power measurement directly at the electrodes, preferably at the rf electrode. The ground connection of the electrical circuit is attained by capacitive coupling of the surroundings and the grounded ring electrode, when present, accounts only partly for the ground connection. The experimental set-up in this work, however, does not allow power measurement directly at the rf electrode.

Comparing the results of both methods one has to take into account that the absorption method does not distinguish the molecules produced in the active plasma region from those produced in the remaining volume of the multi-pass cell, while with OES the molecules exclusively in the glow regions are detected. Moreover, the densities of electronically excited states of molecules measured in emission depend not only on densities of the ground state measured in absorption but also on the electron energy distribution function. Hence, simultaneous measurements in absorption and emission can contribute to a deeper insight into the subject [16].

6. Conclusion

The absolute production rate of the NO molecules by an APPJ is measured for the first time by means of the TDLAS technique. The APPJ is operated at rf (13.56 MHz) in argon (5 and 10 slm) with small (up to 1%) admixtures of argon (1–100 sccm). To allow absorption measurements the plasma source was implemented in a multi-path cell with 100 m optical path length.

The resulting NO production rate is in the range (0.1–80) \times 10^{-3} sccm or (0.05–35) \times 10^{18} molecule s^{-1}. The NO production rate (i) grows with applied power, (ii) has a maximum at 0.2–0.3% of air admixture and (iii) is nearly independent on the Ar flow.

Absorption measurements in the closed volume of the multi-pass cell without ground ring electrode are correlated with emission measurements with the APPJ propagating into ambient air and ground electrode attached. It is shown that the NO emission multiplied with the total jet flow represents the production rate of NO at least at small air admixtures. The similar relative dependences of absorption and emission signals can be exploited as an indication for comparable experimental conditions under different experimental situations. It is concluded for the plasma source under investigation that the NO production rate determined in a closed volume of the multi-pass cell can be used as a measure for the NO production rate in ambient air too. Yet, the different background gas composition as present in the closed measuring volume must be carefully considered.

The electrode configuration related to earth potential influences the balance between the rf power coupled into the discharge and dissipated elsewhere (transmission line, network, stray capacitances) significantly. Thus, maintaining the exact electrode configuration is critical for the compatibility of experimental conditions. A direct measurement of the fraction of power coupled into the plasma alleviates the characterization of the existing conditions and would improve the present set-up where just the generator reading is monitored.

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References


