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Temperature and NO density measurements by LIF and OES on an atmospheric pressure plasma jet

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Abstract. Laser Induced Fluorescence (LIF) is used to determine the density and rotational temperature of the nitric oxide (NO) X ground state in an microwave plasma jet. The jet is operated in ambient air with a flow of helium mixed with 0–6% air. The applied microwave power is 18–55 W. The obtained temperatures are compared with rotational temperatures of the NO A excited state and the N₂ C state, obtained with Optical Emission Spectroscopy. The temperatures obtained with OES are found to be approximately 30% higher than those obtained with LIF. This suggests that the common assumption that the rotational distribution of the excited state is thermalized within the effective lifetime might not be correct. The absolute density of NO X is measured in situ with 1 mm spatial resolution, and is found to have a maximum of about $1.4 \cdot 10^{22} \text{ m}^{-3}$. 
1. Introduction

Nitric oxide (NO) is a chemically active species, that plays a vital role in many physiological processes inside living organisms [1, 2, 3]. Consequently the generation of NO in atmospheric plasmas is an important topic in biomedical plasma applications, for example in the upcoming field of wound treatment [4].

The NO production rate in an atmospheric pressure plasma jet has been measured by Pipa et al using absorption spectroscopy [5] and optical emission spectroscopy [6]. In this case the plasma effluent is collected in a multi-pass cell to measure NO. Even NO detectors are on the market (see Kühn et al [7]). However all these techniques do not allow in situ spatially resolved NO measurements, which is possible by laser induced fluorescence (LIF). Diagnostics of NO using LIF are well established in the field of combustion [8, 9] and in low pressure air plasmas [10, 11]. Using LIF, NO is investigated to determine the density, but also NO is utilized to probe the gas temperature [12]. However LIF measurements on NO in atmospheric pressure non-equilibrium plasma jets are surprisingly scarce.

NO production methods have been studied in combustion systems (see for example [13]). The most important mechanism produces so-called thermal NO, through the Zel’dovich reactions, given by,

\[
\begin{align*}
N_2 + O &\rightarrow NO + N \\
N + O_2 &\rightarrow NO + O
\end{align*}
\] 

These reactions have strong temperature dependencies. Other mechanisms require the presence of hydrocarbons and other fuel related species, and are thus not applicable in our case. In low pressure plasmas it has been shown that reaction (1) is dominant, especially where the N\(_2\) is in an excited state, either electronically (N\(_2\) A\(^\text{3}\Sigma\)) or vibrationally (N\(_2\) X, \(v \geq 12\)) [10, 11]. In atmospheric pressure corona and DBD discharges it has been argued that the reaction (2) is more dominant [10].

In this paper we present measurements of NO in an atmospheric pressure plasma microwave jet operated with a mixture of helium and a few percent of air. NO is normally more abundantly produced at elevated temperatures. For this reason a microwave jet is used for the in situ NO measurements. Note that microwave jets are also used for this specific reason in the plasma medicine field [7]. The absolute density of NO is measured with laser induced fluorescence (LIF). The absolute calibration is performed with a predefined mixture with a known concentration of NO. Since the calibration measurements are performed without plasma, it is imperative to correct the results in the plasma for variations of temperature and collisional quenching, which is important at atmospheric pressure. The temperature is determined using different methods: LIF, optical emission spectroscopy (OES) of NO and N\(_2\), and with a thermocouple. To obtain the quenching we measured the time resolved LIF signal.

The NO is excited from the NO \(X^2\Pi\) ground state with vibrational number.
\( v = 0 \), to the NO \( A^2\Sigma^+ (v = 0) \) excited state. The excitation is done with a UV laser beam around 226 nm. We detect the fluorescence signal from the transition from the NO \( A^2\Sigma^+ (v = 0) \) excited state to the NO \( X^2\Pi (v = 2) \) ground state around 247 nm. The same vibrational transition is measured in the OES measurements of NO.

The experimental setup is explained in the following section. The NO rotational distribution is treated in section 3. The LIF and OES methods are discussed in sections 4 and 5 respectively, including the fitting method used to determine the rotational temperature. The results of the temperature measurements are presented in section 6, followed by the results of absolute density measurements in section 7, and the conclusion in section 8.

2. Experimental setup

2.1. Plasma Source

The plasma source is a microwave jet operated in open air. A gas flow of 6 slm He plus dry air ranging from 0–0.4 slm (0–6%) is flowed through a tube with 12 mm inner diameter. This results in a flow speed of \( 0.9 \text{ ms}^{-1} \). The tube is grounded, while in the center of the tube there is a pin electrode, connected to a microwave generator (2.45 GHz). The forward and reflected microwave power is measured with two thermal head detectors connected to a directional coupler. See figure 1. The power to the plasma (forward minus reflected) ranges from 18–55 W. More details on the source can be found in [14].

The plasma is mounted on a movable table, in order to perform diagnostics at different positions in the plasma.

2.2. LIF setup

The excitation of NO is performed with a high repetition rate UV laser system tunable from about 221–227 nm. A Sirah Cobra dye laser with a Coumarin 2 dye is used, pumped by a YAG-laser at 355 nm (Edgewave IS6III-E). The light from the dye laser is frequency doubled with a BBO crystal. The schematic of the system is shown in figure 2. The laser beam is used unfocussed in order to avoid saturation (see
Figure 2: Experimental setup with plasma jet, a LIF system consisting of a dye laser system and a detection system with monochromator and photomultiplier (PMT), and an OES system consisting of a spectrometer with a CCD camera.

section 4.5), but is narrowed with a pinhole to a size of about 1 mm in diameter. The system operates at 4000 Hz, with a typical pulse energy of the narrowed beam of 1 µJ (maximum around 10 µJ) and a pulse width of 6 ns. The bandwidth of the laser light is 1.4 pm, according to the laser specifications. The laser energy is measured with an Ophir PD10 photodiode energy sensor, that measures the pulse energy of each laser pulse individually at 4 kHz repetition rate.

The fluorescence light is collected perpendicularly to the laser beam by two quartz lenses and focused onto the entrance slit of a UV monochromator. The monochromator is a McPherson 234/302 with 0.2 m focal length and a range of 50–500 nm. The maximum wavelength resolution is 0.2 nm FWHM, the bandwidth can be controlled by setting the slit widths. The entrance slit is perpendicular to the direction of the laser beam in order to minimize the detection volume for maximum spatial resolution. The size of the laser beam and the focusing optics lead to a detection volume of about 1 mm$^3$.

The signal transmitted through the monochromator is detected by a photomultiplier (Hamamatsu R8486), which is optimized for UV wavelengths. The photomultiplier signal is amplified by an Ortec 1 GHz pre-amplifier and led to a computer with a Fast Comtec P7888 time digitizer card, which counts the pulses with a time resolution of 1 ns. Because the photomultiplier is used in photon counting mode, the detection system is easily saturated. This is prevented by controlling the amount of light by adjusting the entrance slit of the monochromator. The bandwidth of the measured signal is controlled by the combination of entrance and exit slit.

To synchronize the laser and the detection system an external trigger pulse is used, generated by a BNC 575 pulse/delay generator. The laser energy sensor is also connected to the computer, to match the data of the pulse counting with the
Figure 3: Time and wavelength resolved LIF signal of microwave jet plasma He + 3% air, 30 W microwave power, measured at 5.0 mm above the tube end.

Figure 4: Air concentration in a jet of 6 slm pure He through a tube with 12 mm diameter, measured by Raman scattering at 4 mm above the tube end.

corresponding laser pulse energy data.

Most measurements are performed by scanning the dye laser to measure a rotational spectrum. The detection bandwidth of the laser is small enough to excite a single rotational transition. The detection bandwidth is set to 5 nm, enough to collect a full vibrational band of the fluorescence signal. During a scan of the laser the spectrum is measured. For each point of the spectrum a time resolved histogram of counts is accumulated over a number of laser shots, usually 500–2000. This way we are able to measure time and wavelength resolved simultaneously. The measured spectra are corrected for variations in laser energy due to random fluctuations, and changes in dye efficiency with wavelength. An example of an acquired LIF measurement is shown in figure 3.
2.3. Calibration

For absolute densities the LIF signal has to be calibrated. This calibration is performed by measuring the LIF signal of a known concentration of NO. To that end we used a gas mixture of He with 20.0 ppm NO, obtained from a He-NO mixture supplied by Linde. The mixture is flown through the tube with 6 slm, with the microwave power turned off. Since the jet is in open air, air will diffuse into the jet and dilute the gas.

To be able to quantify the mixing with air we measured the air concentration in a pure He flow by Raman scattering on $N_2$ and $O_2$. The Raman signal was generated with a 532 nm YAG laser system, and detected with a Triple Grating Spectrometer and an iCCD camera. Details of the setup and measurement can be found in [15]. The radial profile of the Raman signal intensity of $N_2$ and $O_2$ in the jet at 4 mm from the tube end is thus a direct measurement of the air entrainment [15]. The signal from the jet was compared to the Raman signal of ambient air to calculate the air concentration in the jet. The result is shown in figure 4. The air concentration in the center of the tube is below 0.1%, which is close to the detection limit of the system used. At this air concentration an NO density decrease due to dilution is negligible, and the oxidation reaction $2NO + O_2 \rightarrow 2NO_2$ is too slow to significantly change the NO density. The LIF calibration measurements are performed even closer to the tube end (1 mm), so that we may safely assume that the NO concentration of the calibration measurement is equal to that of the pre-mixed gas.

2.4. OES setup

Optical emission spectroscopy is performed by collecting light from the plasma with a lens connected to a fiber. The spot size of the collected light is approximately 2 mm in diameter. The light is transported to the entrance slit of a 1 m spectrometer (Jobin Yvon HR1000, range 190–1500 nm). The spectrum is measured with an SBIG CCD camera. One CCD image of a spectrum covers a range of approximately 10 nm. The slit function is obtained with a low pressure mercury lamp, and has a FWHM of 25 pm.

2.5. Thermocouple

As complimentary measurements we used a type K thermocouple to measure the gas temperature outside the plasma zone. The thermocouple can handle a maximum temperature of 700 K. Inside the plasma thermocouples do not work.

3. NO rotational distribution

The structure of NO is well known [16]. In this work we study transitions from the electronic ground state NO $X^2\Pi$ to the electronic excited state NO $A^2\Sigma^+$ and vice
Figure 5: Rotational energy levels of the NO ground state (a) and the excited state (b).

versa. These states are subdivided in vibrational states with vibrational quantum number \( v \) and rotational states with rotational quantum number \( J \). \( J \) is the total angular momentum. NO has an odd number of electrons, so \( J \) is half-integral with values \( J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ... \).

3.1. NO \( X^2\Pi \) ground state

The energy levels of the \( ^2\Pi \) ground state are best described by Hund's case (a). This results in two multiplet components of the \( X \) state, \( ^2\Pi_{1/2} \) and \( ^2\Pi_{3/2} \), each with their own set of \( J \) values, separated with a relatively large spin-orbit splitting energy. The energy of the rotational states in the NO \( X^2\Pi \) ground state is given by (see also figure 5a),

\[
E_J = B_v J (J + 1) + K_e, \tag{3}
\]

where \( B_v \) is the rotational constant, with value \( B_v = 1.705 \text{ cm}^{-1} \) for the vibration state \( v = 0 \). \( K_e \) is the electronic energy of the multiplet term that accounts for the spin-orbit splitting, with values \( K_e = 0 \) for \( ^2\Pi_{1/2} \) or \( K_e = 119.9 \text{ cm}^{-1} \) for \( ^2\Pi_{3/2} \). Effects on \( E_J \) of higher order terms of \( J \), and so-called \( \Lambda \)-splitting are neglected.

3.2. NO \( A^2\Sigma \) excited state

The excited state \( ^2\Sigma \) has a different structure, which is described best by Hund's case (b). Instead of the usual \( J \) the energy of the rotational states can better be described using the nuclear angular momentum \( N \), which is related to \( J \) by \( J = N \pm \frac{1}{2} \) for spin-up and spin-down respectively. The energy of the rotational states in the NO \( A^2\Sigma \) excited state is given by (see figure 5b),

\[
E_J = B_v N (N + 1), \tag{4}
\]

with \( B_v = 1.996 \text{ cm}^{-1} \) for the vibrational state \( v = 0 \). \( N \) can take the integral values \( N = 0, 1, 2, ... \). Again higher order terms of \( N \) and \( \Lambda \)-splitting are neglected.
3.3. Transitions

We write the quantum numbers of the NO X lower level as $J_l$ and $v_l$, and in the NO A upper level as $J_u$ and $v_u$. During a transition the rotational number $J$ is bound to selection rules, stating that $\Delta J = 0, \pm 1$. This results in three series of branches of rotational lines: the $P$-branch with the transitions following $J_u = J_l - 1$, the $Q$-branch with $J_u = J_l$, and the $R$-branch with $J_u = J_l + 1$. Due to the multiplet components of the states these branches are subdivided. This subdivision is denoted as $P_{ij}$, where $i$ is the multiplet term of the upper state, with $i = 1$ for $J = N + \frac{1}{2}$ and $i = 2$ for $J = N - \frac{1}{2}$. Similarly $j$ is the multiplet term of the lower state, with $j = 1$ for $^2\Pi_{1/2}$ and $j = 2$ for $^2\Pi_{3/2}$. The same goes for the $Q$- and $R$-branch.‡

Transitions are identified by their branch name and initial rotational number ($J_l$ in case of absorption, and $J_u$ in case of emission). See for example $R_{22}$ (4.5) as indicated in figure 5.§

Each transition has an associated wavelength $\lambda$, and Einstein coefficients for emission $A$ and absorption $B$. These coefficients are imported from a database, which is part of the LIFBASE software written by Luque et al [17]. The line wavelength could be calculated from the energy difference using equations 3 and 4. But in order to avoid having to include higher order terms and converting wavelengths from vacuum to air, necessary to obtain the sub-picometer accuracy, we chose to use the values from the LIFBASE database.

3.4. Rotational distribution

If the rotational states of NO are in equilibrium, they are distributed according to the Boltzmann distribution $f_B$, given by,

$$f_B(T_{\text{rot}}) = \frac{2J + 1}{Z_{\text{rot}}} e^{-\frac{E_J}{k_B T_{\text{rot}}}},$$

(5)

where $T_{\text{rot}}$ is the rotational temperature, $k_B$ the Boltzmann constant and $E_J$ the rotational energy given by equation 3 or 4. $Z$ is the rotational partition function, given by [16],

$$Z_{\text{rot}} = \sum_J (2J + 1) e^{-\frac{E_J}{k_B T_{\text{rot}}}} \approx \frac{k_B T_{\text{rot}}}{B_v}.$$  

(6)

In some spectra emission of different vibrational bands overlap. In that case we take into account the vibrational distribution in the Boltzmann factor with vibrational temperature $T_{\text{vib}}$, 

$$f_B(T_{\text{rot}}, T_{\text{vib}}) = \frac{2J + 1}{Z_{\text{rot}} Z_{\text{vib}}} e^{-\frac{E_J}{k_B T_{\text{rot}}} - \frac{E_v}{k_B T_{\text{vib}}}},$$

(7)

‡ In Hund’s case (b) $\Delta N$ is generally used instead of $\Delta J$ for the nomenclature of the branches, but for clarity in this work we always use $\Delta J$ to name the branches.
§ In the case that $i = j$ the branch name is sometimes written as $P_i$ instead of $P_{ii}$. 

Table 1: rate coefficients of Electronic Energy Transfer (EET) and Rotational Energy Transfer (RET) for the NO $A (v = 0)$ state, and Vibrational Energy Transfer (VET) for the NO $X (v = 1)$ state.

<table>
<thead>
<tr>
<th>Species</th>
<th>EET $10^{-16}$ m$^3$s$^{-1}$</th>
<th>RET $10^{-16}$ m$^3$s$^{-1}$</th>
<th>VET $10^{-18}$ m$^3$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.0020$^a$</td>
<td>2.3$^c$</td>
<td>0.013$^e$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.51$^a$</td>
<td>1.7$^d$</td>
<td>0.024$^e$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.0037$^a$</td>
<td>2.9$^d$</td>
<td>0.20$^e$</td>
</tr>
<tr>
<td>air</td>
<td>0.30</td>
<td>2.5$^d$</td>
<td>0.16</td>
</tr>
<tr>
<td>NO</td>
<td>2.49$^b$</td>
<td>4.4$^d$</td>
<td>8.8$^e$</td>
</tr>
</tbody>
</table>

$^a$ Nee et al [18]  
$^b$ Settersten et al [20]  
$^c$ Imajo et al [19]  
$^d$ Lee et al [21]  
$^e$ Calculated from Wysong et al [22] with $T = 295$ K

with $E_v$ the vibrational energy, given by,

$$E_v = \omega \left( v + \frac{1}{2} \right).$$  \hspace{1cm} (8)

The vibrational constant $\omega = 1904$ cm$^{-1}$ for NO $X$ and $\omega = 2374$ cm$^{-1}$ for NO $A$ [17]. The vibrational distribution is only used in relative measurements, which means that $Z_{\text{vib}}$ cancels out in the results, and consequently the value of $Z_{\text{vib}}$ is not important.

4. Laser induced fluorescence

4.1. Two-level model

During a LIF measurement the dye laser is scanned across the transitions of the NO $X (v = 0) \rightarrow A (v = 0)$ band. $n_l$ and $n_u$ are the densities (in m$^{-3}$) of the lower and upper state respectively that are coupled by the laser. The total density of all the rotational states in the NO $X (v = 0)$ ground state is denoted by $n_{\text{gnd}}$ and for NO $A (v = 0)$ we use $n_{\text{exc}}$. The process that populates the upper state is the absorption with the Einstein absorption coefficient $B_{lu}$. Processes that depopulate the upper state are spontaneous emission with Einstein emission coefficient $A_{ul}$, stimulated emission with Einstein coefficient $B_{ul}$, and quenching $Q$.

The quenching $Q$ is the total rate of all collisional processes that depopulate the states from which the fluorescence signal is monitored. These processes include Electronic Energy Transfer (EET, also known as electronic quenching), Vibrational Energy Transfer (VET) and ionization. $Q$ is given by a sum over the species $i$ in the plasma with density $n_i$ (m$^{-3}$) and quenching coefficient $q_i$ (m$^3$s$^{-1}$),

$$Q = \sum_i n_i q_i.$$  \hspace{1cm} (9)
Values of coefficients for EET and VET can be found in table 1. No data seems to exist on VET rates in the excites NO $A$ state, so as an indication relaxation rates of the NO $X$ ($v = 1$) state are given. The electronic quenching is dominant and determines the overall quenching rate (pure N$_2$ being an exception where the VET rate is of the same order). Note that we can determine the value of $Q$ directly from the measurements (see section 4.4) so that VET is automatically included.

Rotational Energy Transfer (RET) is much faster than VET, with a rate of about $6.0 \times 10^9$ s$^{-1}$ in air (and similar for He). This means that RET takes place on timescales smaller than the laser pulse time. However, since the fluorescence of the full vibrational band is monitored, RET does not cause a loss of signal. Therefore it is not included in the quenching.

The absorption coefficient $B_{lu}$ (in m$^2$J$^{-1}$s$^{-1}$) and emission coefficient $A_{ul}$ (in s$^{-1}$) are taken from the LIFBASE database [17]. Here $A_{u}$ is the sum over all transitions to lower states $l$ originating from upper state $u$,

$$A_u = \sum_l A_{ul} = \frac{1}{\tau_0},$$ (10)

where $\tau_0$ is the natural lifetime. In order to avoid carrying out the sum ourselves we use the natural lifetime $\tau_0$, which is available from the literature.

The coefficient for stimulated absorption is given by,

$$B_{ul} = \frac{g_l}{g_u} B_{lu},$$ (11)

where $g$ is the electronic degeneracy ($g_u = 2$ for the NO $A$ state, and $g_l = 4$ for the NO $X$ state).

The measured, time dependent LIF signal $s(t)$ depends on the wavelength range of the detection system, and reads,

$$s(t) = CV n_u(t) A_{uf},$$ (12)

where $A_{uf}$ is the radiative transition probability that belongs to the fluorescence transition, with emission that falls within the detection range. In case the detector covers more than one line the coefficients must be summed as in equation 10. $V$ is the detection volume (m$^3$), and $C$ is a constant factor to take the efficiency of the optics and detector into account.

4.2. Rate equation

The rate coefficients form a rate equation for the upper state,

$$\frac{dn_u}{dt} = B_{lu} n_l - (B_{ul} I + A_u + Q) n_u.$$

$I$ is the arbitrarily shaped laser intensity in Jm$^{-2}$, with total energy $E_I$ in J, $\Gamma$ the overlap integral in s, and laser beam cross-sectional area $a$ in m$^2$, 

$$I(t) = \frac{E_I \Gamma}{a} i(t),$$ (14)
where \( i(t) \) is the arbitrary shape of the pulse in time in \( s^{-1} \), normalized such that \( \int_{-\infty}^{\infty} i(t) \, dt = 1 \).

To simplify the rate equation we make the following assumptions:

(i) The laser intensity is low, and only a small fraction of the NO is excited by the laser. This means that at all times \( n_u \ll n_l \), and \( n_l \) can be considered constant (this assumption is verified in section 4.5).

(ii) The quenching and emission coefficient are independent of the rotational state, i.e. \( Q \) and \( A_u \) are the same for all rotational states in the NO \( A (v = 0) \) band (this is verified in section 4.4).

(iii) The ground state distribution is in equilibrium, i.e. \( n_l = f_B n_{\text{gnd}} \).

Assumption 1 means that stimulated emission can be neglected. Since the ground state density is considered constant, no rate equation is needed for this state. With \( n_l \) constant, RET in the ground state can be neglected. In fact, the refilling of the lower state by RET during the laser pulse even contributes to the assumption 1.

From assumption 2 we can conclude that the decay rate of the excited state is independent of the rotational state. Since the detection system measures the whole NO \( A (v = 0) \rightarrow X (v = 2) \) vibrational band, any change in the rotational distribution does not affect the LIF signal. This means that we only have to regard the total density \( n_{\text{exc}} \) of the excited state NO \( A (v = 0) \), and RET in the excited state can be ignored.

Note that assumption 3 also means that the vibrational states of NO \( X \) are in equilibrium. If the higher vibrational states are populated, this means that the \( n_{\text{gnd}} \) is not necessarily equal to the total NO \( X \) density (see the discussion in section 7.1).

With the above assumptions, equation 13 can be written as,

\[
\frac{d n_{\text{exc}}(t)}{dt} = B_{lu} f_B n_{\text{gnd}} I(t) - (A_u + Q) n_{\text{exc}}(t) \quad (15)
\]

The solution of this equation can be shown to be the convolution of the laser pulse shape \( I(t) \) and an exponential decay,

\[
n_{\text{exc}}(t) = B_{lu} f_B n_{\text{gnd}} \left[ I(t) \otimes e^{-(A_u + Q)t} \right]. \quad (16)
\]

By using equations (12) and (14) and integrating \( n_{\text{exc}} \) in time we can obtain the total time integrated LIF signal \( S \),

\[
S = \int_{-\infty}^{\infty} C V A_u f n_{\text{exc}} \, dt = C l E f n_{\text{gnd}} \frac{A_u f}{A_u + Q} \cdot \Gamma B_{lu} f_B, \quad (17)
\]

where \( l = \frac{V}{a} \) is the detection length along the laser beam. A similar expression is used by Uddi et al [10]. Of these factors only \( f_B, B_{lu} \) and \( \Gamma \) depend on the rotational state. The overlap integral \( \Gamma(\lambda) \) is a function of the laser wavelength \( \lambda \). It contains the spectral line profile, which is composed of the spectral distribution function of the transition and the laser profile. The factors which are independent of the rotational
state can be combined into an intensity factor $F = C E_i n_{\text{gnd}} A_{uf} \tau$, with the decay time $\tau = \frac{1}{A_u + Q}$, thereby reducing equation 17 to,

$$S(\lambda) = F B_{lu} f_B \Gamma(\lambda).$$

(18)

The line profile is approximated by a normalized Voigt profile.

$$\Gamma(\lambda) = G(\lambda, \Delta_G) \otimes L(\lambda, \Delta_L),$$

(19)

where $G$ is a Gaussian profile with width $\Delta_G$ and $L$ is a Lorentzian profile with width $\Delta_L$. To calculate a complete absorption spectrum $P(\lambda)$ consisting of many lines, the individual rotational line intensities $S$ have to be added up,

$$P(\lambda) = F \sum_i B_{lu,i} f_B \Gamma(\lambda - \lambda_i).$$

(20)

where $\lambda_i$ is the wavelength of the transition $i$. The calculated spectrum $P$ can be fitted to a measured spectrum using Matlab to obtain $T_{\text{rot}}$, $\Delta_G$, $\Delta_L$ and the intensity factor $F$ as explained in [23].

4.3. Absolute calibration

The absolute density is obtained by calibrating the LIF intensity in a gas mixture with a known NO concentration at room temperature (in this paper we use helium containing 20 ppm NO). The absolute ground state density $n_{\text{gnd}}$ in the plasma is then calculated with,

$$n_{\text{gnd}} = \frac{n_{\text{cal}} E_{\text{cal}} \tau_{\text{cal}}}{E_{\text{cal}}} \cdot \frac{F}{E_I \tau}.$$  

(21)

$E_I$ and $E_{\text{cal}}$ are measured during the experiment with a laser energy meter to account for fluctuations in the laser intensity between the measurement and the calibration. The difference in quenching is accounted for by measuring the decay time of the LIF signal $\tau$ and $\tau_{\text{cal}}$. We stress the fact that $n_{\text{cal}}$ is equal the total NO density of the calibration gas, since at room temperature all NO is in the ground state (see also section 7.1).

4.4. Quenching

After the laser pulse, the density $n_{\text{exc}}$ decays exponentially with decay time $\tau$. $Q$ can be calculated using equation 9 and the rate coefficients listed in table 1, while $A_u$ is given by the natural lifetime $\tau_0$ of the NO $A$ state (equation 10). The calculated natural lifetime for the $v = 0$ band is $\tau_0 = 205.000 \text{ ns}$ [17], while experimentally a value of $\tau_0 = 192.6 \pm 0.2 \text{ ns}$ has been measured (see [24], also for an overview of other measurements of $\tau_0$).

The decay time can directly be measured by making an exponential fit of the time resolved LIF signal. See for an example figure 6. This time resolved signal is available for each wavelength point in the spectrum, which provides a way to
measure the quenching for each rotational line. The result is shown in figure 7, showing that the decay times are randomly distributed around an average value of $\tau = 53.4 \pm 2.4$ ns. A very small decreasing trend towards higher $J$ might be observed, but this difference falls within the error margin, and can be safely ignored. We may conclude that $\tau$ is constant for the LIF signal of different rotational lines. This conclusion is confirmed by the fact that the pattern of figure 7 is not reproducible in subsequent measurements (not shown). Note that some of the lines overlap with lines of a different branch, and that case we are unable to distinguish between the lines.

From the observation that $\tau$ does not depend on the initial rotational state we cannot conclude that the quenching is the same for each rotational level of the excited NO $A$ state. Most likely RET causes a redistribution of the rotational states of the NO $A$ state before the states decay. With the present measurements we cannot determine the RET in the NO $A$ state, but for the LIF signal it does not matter. The decay time is independent of the rotational state, and equation 17 remains valid.

The calculated decay time corresponding to a gas mixture of He plus 3.2% air at
atmospheric pressure and 1000 K is $\tau = 73 \text{ ns}$. Note that we do not take into account temperature dependence of the rate coefficients. Assuming the rate coefficients at 1000 K are slightly higher than those given in table 1, the measured decay times are consistent with the calculation.

4.5. Linearity

In order to measure NO densities, the LIF signal must not be saturated. This means that $n_u \ll n_l$ so that stimulated emission can be neglected. This can be checked by measuring if the fluorescence signal is proportional to the energy of the laser pulse. This measurement has been performed on a gas flow of He at atmospheric pressure, with 20 ppm NO. The results are shown in figure 8. The measurements in this work are performed with laser energies around 1 µJ, which is in the linear regime. The LIF signal therefore is considered not saturated.

5. Emission spectroscopy

In the calculation of an emission spectrum, we make the assumptions that the rotational distribution of the excited state is in equilibrium, i.e. $n_u = f_B n_{\text{exc}}$.

The measured signal is given by,

$$S = CVA_{uf''} f_B n_{\text{exc}}$$

where $f_B$ and $A_{uf}$ depend on the rotational state. The emission spectrum $P(\lambda)$ can be obtained using equation 20. The temperature of the excited state can be obtained by fitting the spectrum with fitting parameters $T_{\text{rot}}$ and $T_{\text{vib}}$ [23].
Temperature and NO density of an atmospheric pressure plasma jet

6. Temperatures

The temperature of the plasma is determined in a number of ways. The rotational temperature of NO X is measured by LIF, and of NO A with OES. Furthermore we measured the rotational temperature of N₂ by OES, and applied a thermocouple in the afterglow of the plasma.

6.1. NO X rotational temperature

Figure 9 shows an example of a LIF excitation spectrum of NO, measured by scanning the dye laser over the rotational states of the NO X complex. The spectrum is recorded in the afterglow of the plasma, where there is almost no plasma emission. LIF measurements inside the plasma are corrected for background plasma emission. The rotational temperature is determined by the fitting procedure as described in section 4.2 and reference [23]. The fit includes all rotational lines in the wavelength range, 118 in total with \( J \) ranging from 1.5–31.5. Similar spectra were measured at...
6.2. NO A rotational temperature

The rotational temperature of the NO A excited state is determined with an emission spectrum measured with OES. An example of an NO spectrum in the range 240–248 nm is shown in figure 11, with temperature fit (section 5). The measured vibrational transition NO A \((v = 0) \rightarrow X (v = 2)\) is equal to the detected fluorescence of the LIF measurements. There is an overlapping contribution of the NO A \((v = 1) \rightarrow X (v = 3)\) band — best visible as a bump in the spectrum around 243–244 nm — which is not present in the LIF spectrum. Therefore the Boltzmann factor of equation
Figure 13: OES spectrum of N\textsubscript{2} second positive system, measured in a 30 W plasma at 2 mm above the tube. The fitted temperature $T_{\text{rot}} = 1730$ K.

Figure 14: Axial temperature profile of the plasma jet obtained by fitting OES spectra of N\textsubscript{2}, at different values of microwave power. See figure 13 for an example fit.

7 has been used and the spectrum has been fitted with the vibrational temperature as extra fit parameter. The fitted $T_{\text{vib}}$ is considerably higher than $T_{\text{rot}}$.

The temperature profiles of different microwave powers are shown in figure 12. The NO is chemically produced in the plasma, and depending on the production method the NO could be produced in an excited state. This could lead to deviations of the measured rotational temperature from the gas temperature. Therefore the same procedure is applied to a spectrum of N\textsubscript{2}, a species that is already present in the gas mixture and is known to be reliable for gas temperature measurements at atmospheric pressure [25]. Figure 13 shows an example of the N\textsubscript{2} C $\rightarrow$ B band, the second positive system around 337 nm. Axial temperature profiles are given in figure 14. The temperatures are slightly lower than the NO temperatures.

6.3. Thermocouple

As a complimentary measurement to validate the other measurements we used a thermocouple to measure the temperature in the afterglow of the plasma. The results are shown in figure 15.
6.4. Interpretation of rotational temperature

Rotational energy transfer is mainly caused by collisions with heavy particles and it is often assumed to be fast enough such that the rotational distribution is in equilibrium with the translational energy distribution of the heavy particles. This assumption is confirmed by the NO RET rates (table 1). However, these rates are known at low temperature, but to the authors knowledge no experimental data exists for temperatures above 1000 K. Furthermore these are state-to-state rates, and little information is available on the time it takes to completely thermalize the rotational distribution. Lee et al [21] mentions a thermalization time of ‘less than 0.5 ns’ for NO in ambient air, at atmospheric pressure and room temperature. No experimental data seems to exist for higher temperatures.

A thermalization time of 0.5 ns would be much faster than the effective lifetime of the state (about 50 ns). This suggests that the NO A rotational states (as well as the NO X states) have a Boltzmann distribution, and can be used to measure the gas temperature.

Figure 16 shows an overview of the temperature measurements at a microwave power of 30 W. The OES measurements show a good agreement with each other, but are high comparable to the LIF measurements. This difference suggests that the excited state is not fully thermalized, although the shape of the OES spectrum resembles a Boltzmann distribution.

OES is a line-of-sight technique, while LIF is a localized measurement. The obtained temperatures thus do not result from the same plasma region. However, all measurements agree that the plasma is the hottest in the core. The OES measurements — which include the cooler outer regions — are thus underestimating the core temperature. The difference between the OES and LIF measurements therefore cannot be explained by the difference in spatial information.

A possible explanation could be found in the excitation mechanism in the plasma. Excitation through electron collision from the ground state is likely to play
a large role, and in this case the NO is electronically excited without changing the rotational distribution. The distribution of the ground state is copied to the excited state. But due to the difference in rotational constant $B_v$ this yields a change in the rotational temperature. In the limit where RET is completely neglected this results in,

$$T_{\text{exc}} = \frac{B_{v,\text{exc}}}{B_{v,\text{gnd}}} T_{\text{gnd}} = 1.17 T_{\text{gnd}}$$  \hspace{1cm} (23)

A similar effect has been described for H$_2$ [26]. This could partly explain the difference found between the temperatures of the NO OES and LIF measurement. However, one would expect the excited NO that is responsible for producing the OES has an effective lifetime that is comparable to the lifetimes found in the LIF experiments. In that case the lifetime is long enough such that RET does play an important role. Furthermore, the effect does not explain the high temperatures found in the N$_2$ OES measurements.

Note also that the error bars for the laser scan measurements are relatively large. This is due to the fact that individual rotational peaks in the spectrum do not fit perfectly to the theoretical Boltzmann distribution (see figure 9), but show deviations in intensity of up to 10%. Part of these deviations can be contributed to fluctuations in the plasma during the measurements.

The vibrational temperatures from the OES measurements are much higher than the rotational temperatures. This can be understood by the way the vibrational energy transfer happens, namely mostly by electron collisions. The electrons have a much higher temperature, typically in the order of 1 or 2 eV [15]. Consequently $T_{\text{vib}}$ can be much higher than the heavy particle temperature.

So which rotational temperature is the best approximation of the gas temperature? Most likely the NO $X$ rotational distribution is the best choice, due to the longest effective lifetime. There is no reason to assume a non-Boltzmann
distribution in the ground state. The NO X temperatures measured by LIF are confirmed in the afterglow by the thermocouple. However, the NO A temperatures measured by OES are confirmed by the N2 OES. Although the N2 rotational spectrum is known to be used for determining the gas temperature, the exact excitation mechanisms of the N2 C state in our plasma conditions are not known. Further research is needed.

A simple estimate of the gas temperature based on the flow rate (6.0 slm He and 0.2 slm air), the applied power (30 W) and the specific heat of He ($c_p = 20.79 \text{ J mol}^{-1}\text{K}^{-1}$) and air ($c_p = 29.1 \text{ J mol}^{-1}\text{K}^{-1}$) results in a gas temperature rise $\Delta T = 344 \text{ K}$. This is much lower than the measured temperatures in the plasma core, which means that the gas is not uniformly heated.

7. Absolute NO density

We measured the absolute density of the NO X ($v = 0$) ground state employing equation 21. The absolute calibration was performed by flushing 6.0 slm helium with 20.0 ppm NO through the tube. Figure 17 gives an examples of the LIF signals corresponding to a calibration measurement and a measurement inside the plasma. The spectra include 26 absorption lines — some of which overlap — with $J$ in the range 1.5–35.5.

Figure 18 shows a contour plot of the axially and radially resolved density of NO X ($v = 0$). The NO density has a dip in the plasma core, and a maximum of $1.3 \cdot 10^{21} \text{ m}^{-3}$ at the edge of the optical emission zone of the plasma. The decreased density in the core can largely be explained by the gas expansion due to higher temperatures.

Measurements under the same condition, performed on separate days show a repeatability better than 20% variation in density. This variation is largely due to the plasma stability and accuracy of the plasma power measurements.

Figure 19 shows axial profiles measured radially at the center of the plasma, at different values of the microwave power and different values of air concentration mixed into the helium. The NO density increases with power, but saturates at about 30 W. The axial position of the maximum shifts to a higher position with increasing power. This is due to the fact that the size of the plasma increases. The edge of the optical emission zone shifts from 3 to 6 mm as the power increases from 18 to 55 W, as can be seen from the emission (figure 12). The maximum NO density is approximately linear with the premixed air concentration. At higher air concentration the plasma size decreases, and it becomes more difficult to sustain the discharge.

The decay time $\tau$ calculated from the same measurement data is shown in figure 20. Inside the plasma the quenching is high (low $\tau$), and decreases in the plasma afterglow. At even higher axial positions, the quenching increases again, because of the mixing with ambient air (oxygen is a much higher quencher than helium, see
Figure 17: Examples of LIF spectra used to measure the NO density, with fit. (a) shows the spectrum of the calibration measurement, with fitted temperature $T_{\text{rot}} = 336 \pm 12$ K. (b) shows the (background corrected) spectrum inside the plasma at 30 W with 3% air, with fitted temperature $T_{\text{rot}} = 1377 \pm 122$ K.

The increase of quenching due to the increase of air is also visible in the figure 20b and is especially pronounced in the case of pure He flow, as expected.

7.1. Temperature effects on density

In principle the density is corrected for temperature variations through the Boltzmann factor, which is included in the fitting procedure. However, as shown in section 6, there is a large uncertainty in the temperature, depending in the used method. The temperatures used in the density calculations are the ones obtained from the NO LIF measurements itself. Calculations of the combined Boltzmann factor of the absorption lines in the measured spectral range show that a temperature error
Figure 18: Axial and radial NO \( X (v = 0) \) density in a 30 W plasma with 3% air, measured with LIF.

Figure 19: NO \( X (v = 0) \) ground state density with (a) different microwave powers (air concentration 3.2%), and (b) different air concentrations (power 30 W).
The obtained densities are those corresponding to the lowest vibrational state $v = 0$. The population of the higher vibrational states is not measured. Unlike the NO $A$ excited state, the lifetime of the NO $X$ ground state is most likely long enough such that the vibrational states are in equilibrium. According to equation 7 the fraction $\frac{n_{X,v=1}}{n_{X,v=0}} = 9.2 \cdot 10^{-5}$ for $T_{vib} = 295$ K, meaning that at room temperature the $v = 1$ population is negligible. But in the plasma with $T_{vib} = 1500$ K the fraction becomes $\frac{n_{X,v=1}}{n_{X,v=0}} = 0.16$. Interpreting the NO $X$ ($v = 0$) density as the total NO $X$ ground state density could lead to an underestimation up to 16%. Furthermore, due to collisions with electrons with an electron temperature typically in the order of 1 or 2 eV [15], $T_{vib}$ can have values much higher than the heavy particle temperature. This leads to even higher populations of the NO $X$ ($v = 1$) state, up to 33% for $T_{vib} = 2500$ K.
8. Conclusion

We have shown a comparison of temperature measurements between LIF and OES measurements, which translates as a comparison of the rotational temperatures of the NO X versus the NO A state. The OES temperatures are found to be approximately 30% higher than the LIF temperatures. This suggests that the common assumption that RET is fast enough to thermalize the rotational states in the excited states might not be true for all plasma conditions. OES measurements of NO and N\textsubscript{2} are well in agreement. The longer effective lifetime of the NO X compared to the NO A state suggests that the temperatures obtained by LIF are more reliable than the OES temperatures of NO. However, it is not fully understood why the OES temperatures of N\textsubscript{2} have the same high values as for NO. Note that the LIF temperature measurements have been performed with a fit of 118 rotational lines, much more than in other multi-line methods.

The density of NO has been measured with LIF at different positions in the plasma and with varying microwave power from 18–50 W and air concentration from 0.0–6.3%. The maximum NO X density is in the afterglow, above the brightest part of the plasma. This can largely be explained by the expansion of the gas due to higher temperatures in the plasma core. With higher power the plasma size increases, and so does the position of the maximum density. The density increases with the plasma power, but seems to saturate above 30 W at about 1.4 \cdot 10^{21} \text{ m}^{-3}. The density increases linearly with the air concentration in the investigated concentration range.

Close to the plasma the temperature is too high to be used for the treatment of tissue or other heat sensitive materials. However we must note that significant NO densities remain present of the far afterglow at gas temperatures below 500 K. This would allow the jet to be used for treatment of heat sensitive materials.


Temperature and NO density of an atmospheric pressure plasma jet


