Thermalization of rotational states of NO A2Σ+(ν = 0) in an atmospheric pressure plasma

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Thermalization of rotational states of NO $A^2\Sigma^+(v = 0)$ in an atmospheric pressure plasma

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Laser induced fluorescence (LIF) measurements of nitric oxide (NO) are performed in an atmospheric pressure microwave plasma jet, operated with a mixture of He and 3% air. The fluorescence signal of NO $A^2\Sigma^+(v = 0)$ is measured time and fluorescence wavelength resolved. Based on the evolution of the rotational spectrum at different positions in the plasma, we determined the thermalization time of the rotational distribution of NO A after pumping a single transition, at temperatures in the range 300–1500 K. Also, a LIF-RET (rotational energy transfer) model is developed to simulate the RET and to calculate the thermalization time. The RET rate coefficients are calculated using the energy corrected sudden-exponential power scaling law. It was found that it is necessary to take the fine structure of the rotational states into account. At room temperature the results of the measurement and the simulation are consistent, and the thermalization occurs during the laser pulse (11 ± 1 ns). At elevated temperatures the measurements show a large increase in thermalization time, up to 35 ± 4 ns at 1474 K. This time is much longer than the laser pulse, and of the order of the NO A lifetime. This means that for spectroscopy measurements of the rotational states of NO A, the RET has to be taken into account to derive gas temperatures from the rotational distribution of NO A.

I. INTRODUCTION

Nitric oxide (NO) is an important species in many fields, such as combustion (micro-)biology, and atmospheric chemistry. Its destruction and oxidation are studied in environmental remediation studies, such as air purification. Also in medicine it is an interesting species which is believed to be a key ingredient in plasma induced wound healing. In combustion, NO has been extensively studied by laser induced fluorescence (LIF). The density and production mechanisms of NO are studied, but NO is also used as a molecule to probe the temperature by LIF in flames.

NO is a relatively heavy molecule, compared to other common diatomic species like OH and CH. The rotational constant $B_0 = 2.00 \text{ cm}^{-1}$ for the NO $A^2\Sigma^+$ excited state is low compared to 17.39 cm$^{-1}$ for OH $A^2\Sigma^+$ and 14.90 cm$^{-1}$ for CH $A^2\Delta$. As a consequence, the energy separation between neighboring rotational states is smaller and the rotational states of NO are believed to thermalize very fast. The rotational distribution is close to equilibrium and is often assumed to obey a Boltzmann distribution. The rotational energy transfer (RET) within a vibrational band happens mainly through collisions with atomic and molecular species in the buffer gas. Therefore, the rotational temperature of NO A is thought to be a good approximation of the gas temperature (the translational temperature of the atomic and molecular species). While the rotational relaxation of OH A has been studied in considerable detail, not much data exist on the thermalization time of the rotational states of NO. Lee et al.

mention a thermalization time “less than 0.5 ns” for the NO A state at 300 K and atmospheric pressure.

In this work, we study the thermalization of rotational states of the NO $A^2\Sigma^+(v = 0)$ excited state by LIF. We excite a rotational transition from the NO $X(v = 0) \rightarrow A(v = 0)$ band, and with a spectrometer we measure the fluorescence signal from the NO $A(v = 0) \rightarrow X(v = 0)$ band and wavelength resolved. This way we are able to follow the evolution of the rotational emission spectrum of the NO A state, and we can determine the thermalization time of the rotational distribution of NO A ($v = 0$).

The thermalization time of the rotational states depends on the RET rates. For NO, the RET is well studied. Rate coefficients for the NO A excited state have been measured by several groups for different molecular and atomic gases: NO, N$_2$, O$_2$, and He and Ar. These measurements include total rate coefficients from the excitation of one rotational level, and state-to-state rate coefficients. However, not all rotational levels have been investigated, and also the temperature dependence is still largely unknown, especially at higher temperatures. To fill in the gaps in the measurements, several empirical scaling laws have been described to determine the rate coefficients. These scaling laws contain fit parameters, which have to be fitted to the experimental values.

Furthermore, in these scaling laws the fine structure of the NO A state has not been taken into account. NO $A^2\Sigma^+$ is described by Hund’s case (b). It has a fine structure with states $F_1$ and $F_2$. OH has a structure comparable to NO, and for OH $A^2\Sigma^+$ the rate coefficients have been measured and calculated with the fine structure taken into account (see Kienle et al.). It was found that for OH the fine structure

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conserving transitions \( (F_1 \rightarrow F_1 \) and \( F_2 \rightarrow F_2 \)) have much higher rate coefficients than transitions where the fine structure changes \( (F_1 \leftrightarrow F_2) \).

These slow fine structure changing transitions are relatively unimportant while measuring the state-to-state rate coefficients of NO A, but in determining the thermalization time they could very well be the time determining processes. Indeed, in LIF measurements the pumping of the excited states is generally not equally distributed between the \( F_1 \) and \( F_2 \) states. So to thermalize the population a transfer between \( F_1 \) and \( F_2 \) is needed, and if this process is slow, so will the thermalization time be.

In Sec. II, we describe a rotational level model to simulate the RET of NO A. The RET rate coefficients of the NO A state are calculated using the energy corrected sudden-exponential power (ECS-EP) law that has previously been used for OH A, with the fine structure taken into account. In Sec. III, we present experimental results of the wavelength resolved LIF. Results are given of the thermalization time of NO A \( (v = 0) \) in a plasma at atmospheric pressure with temperatures in the range 300–1500 K. In the conclusion (Sec. IV), the unexpected effects of thermalization on the rotational levels on LIF of NO in the context of LIF as a gas temperature diagnostic are discussed.

II. LIF-RET MODEL

To discuss the effects of different processes that populate and depopulate the rotational states, we introduce an LIF-RET model, as schematically depicted in Figure 1. We consider two vibrational bands, the ground state NO \( X (v = 0) \), where \( v \) is the vibrational number, and the excited state NO \( A (v = 0) \). In this work, we identify the rotational states by the nuclear angular momentum \( N = 0, 1, 2, \ldots \), because in the NO A state the rotational state energy depends on \( N \), rather than the rotational number \( J \). \( J \) is related to \( N \) by \( J = N + \frac{1}{2} \) for \( F_1(N) \), and \( J = N - \frac{1}{2} \) for \( F_2(N) \). The rotational states in the NO \( X (v = 0) \) band are denoted with \( p \) ranging from 1 to \( m \). Similarly, the NO \( A (v = 0) \) band consists of rotational states \( q \). Finally, there is a reservoir state \( r \) that acts as a reservoir of all other NO states. The total number of levels considered in the model is thus \( 2m + 1 \). We took into account all rotational levels up to \( N = 80 \), so \( m = 160 \).

A. Rate coefficients

The processes that populate and depopulate the levels in the model are: laser absorption \( B_{pq} \), spontaneous emission from the upper to the lower state \( A_{qr} \), and from the upper state to the reservoir state \( A_{qr} \); quenching from the upper state \( Q_{qr} \); rotational energy transfer between the levels of the lower state \( R_{pp'} \), and the upper state \( R_{qq'} \); and de-excitation from the reservoir state to the ground state \( D_{rp} \). We will discuss these processes one by one.

1. Absorption and stimulated emission

The laser wavelength is tuned to one specific transition. The absorption rate \( B_{pq} \) is given by the Einstein absorption coefficient \( B_{pq} \) in \( m^2 J^{-1} s^{-1} \) and the laser intensity \( J \) in \( J \) \( s^{-2} \) \( m^{-2} \). The absorption coefficients of the levels \( p \) and \( q \) that are coupled by the laser are taken from the LIFBASE database. The laser beam cross-sectional area in \( m^2 \); and \( t(t) \) is an arbitrary time-dependence of the pulse shape in \( s^{-1} \), normalized such that \( \int_{-\infty}^{\infty} i(t)\,dt = 1 \).

The stimulated emission rate \( B_{qp} \) can be calculated with

\[
B_{qp} = \frac{g_p}{g_q} B_{pq},
\]

where \( g \) is the electronic degeneracy (\( g_q = 2 \) for NO A, and \( g_p = 4 \) for NO \( X \)).

2. Spontaneous emission

The state-to-state emission coefficients \( A_{qp} \) in \( s^{-1} \) from initial level \( q \) in the NO \( A (v = 0) \) band to final level \( p \) in the NO \( X (v = 0) \) band are taken from the LIFBASE database.

The emission to all other levels is modeled as the emission from the upper state to the reservoir state \( A_{qr} \). This is calculated by subtracting the state-to-state coefficients in the model from the total emission rate, given by the upper state natural lifetime \( \tau_0 \).

\[
A_{qr} = \frac{1}{\tau_0} - \sum_p A_{qp}.
\]

The calculated natural lifetime for the NO \( A (v = 0) \) band is \( \tau_0 = 205.000 \) ns, while experimentally a value of \( \tau_0 = 192.6 \pm 0.2 \) ns has been measured. The latter is used in this work.

3. Quenching

The quenching \( Q_{qr} \) from the NO \( A (v = 0) \) state is given by a sum over the species \( k \) in the plasma with density \( n_k \) \( (m^{-3}) \) and quenching coefficient \( q_k \) \( (m^3 \) \( s^{-1}) \),

\[
Q_{qr} = \sum_k n_k q_k.
\]
TABLE I. Rate coefficients for NO A. The RET rates are the total rates from all transitions originating from one rotational state \( N_q \) indicated between brackets.

<table>
<thead>
<tr>
<th>Species</th>
<th>Quenching ( 10^{-16} \text{ m}^3 \text{s}^{-1} )</th>
<th>RET ( 10^{-16} \text{ m}^3 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.0020(^a)</td>
<td>5.23(^b) (7)</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>1.51(^a)</td>
<td>2.24(^a) (5)</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>0.0037(^a)</td>
<td>3.37(^a) (5)</td>
</tr>
<tr>
<td>Air</td>
<td>1.22</td>
<td>3.14 (5)</td>
</tr>
<tr>
<td>NO</td>
<td>2.49(^d) (mean)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Nee et al.\(^5\)
\(^b\)Imajo et al.\(^6\)
\(^c\)Lee et al.\(^4\)
\(^d\)Setersten et al.\(^6\)

The rate coefficients \( k_q \) are known from literature, see Table I. To the authors’ knowledge no data exist on rotational state dependent quenching rates. We therefore assume all rotational states having identical quenching.

4. Rotational energy transfer

The state-to-state rotational energy transfer rates \( R_{qq'} \) from initial state \( q \) to final state \( q' \) are given by

\[ R_{qq'} = n_k k_{qq'}, \]

where \( n_k \) is the density of species \( k \) in the buffer gas, \( k_{qq'} \) are the state-to-state rate coefficients. Several scaling laws exist to calculate \( k_{qq'} \), we use the energy corrected sudden (ECS) approximation, as employed for \( \text{OH} A^2\Sigma^+ \) by Kienle et al.\(^6\) The scaling law has been used previously for NO A by Imajo et al.,\(^6\) but without including the fine structure. The ECS scaling law requires a set of rate coefficients \( k_L \) as input, which is provided by the exponential power (EP) scaling law, hence the name ECS-EP.

With the ECS law we calculate the rate coefficients \( k_{qq'} \) for the exothermic rotational transitions \( q \rightarrow q' \) where \( E_q \geq E_{q'} \). State \( q \) is characterized by \( N \) and \( J \), and state \( q' \) by \( N' \) and \( J' \). For NO A the energy \( E_q \) of state \( q \) is given by

\[ E_q = B_v N (N + 1), \]

with \( B_v = 1.996 \text{ cm}^{-1} \) the rotational constant of the NO \( A (v = 0) \) state. The ECS scaling relation for \( k_{qq'} \) is then

\[ k_{qq'} = (2J' + 1) \sum_{L=N-N'} M_{L}^{qq'} |A_{L}^{NN'}|^{2} k_{L}. \]

\( M_{L}^{qq'} \) is the angular momentum coupling coefficient,

\[ M_{L}^{qq'} = (2L + 1) \left( \frac{J'}{L} \right)^{2} \left( \frac{J}{2} \right) \left( 1 - \epsilon \epsilon' (-1)^{J+J'+L} \right), \]

where \( \epsilon = 1 \) for \( F_1 \) and \( \epsilon = -1 \) for \( F_2 \), and \( \left( \begin{array}{c} J' \cr L \cr J \end{array} \right) \) is the Wigner 3-j symbol. The adiabaticity factor \( A_{L}^{NN'} \) is given by

\[ A_{L}^{NN'} = \frac{6 + \left( \frac{E_{L}}{2kT} \right)^{2}}{6 + \left( \frac{E_{L}}{2kT} \right)^{3}}, \]

where \( \Delta E_{L} = 0 \) for \( L = 0 \), and \( \Delta E_{L} = E_{L} - E_{L-1} \) otherwise (and similar for \( \Delta E_{N} \)). \( \epsilon \) is a fitting parameter, the so-called interaction length; and \( \epsilon_{\text{th}} = \sqrt{8kT/\pi \mu} \) is the thermal velocity, with \( \mu \) the reduced mass of the NO molecule and \( H \) as main background gas (at room temperature \( \epsilon_{\text{th}} = 1337 \text{ ms}^{-1} \). Ref. 10). Note that indeed the RET is dominated by He induced RET as can be derived from Table I.

This scaling law uses \( k_L \) as input, with \( L = 1, 2, \ldots, N + N' \). \( k_L \) is defined as the rate coefficient for the transition \( F_1(L) \rightarrow F_1(0) \). These rate coefficients are calculated using the EP scaling law, which is a combination of the exponential gap law (EGL) and the statistical power gap (SPG) scaling laws. \( k_L \) is given by

\[ k_L \equiv k_{F_1(L) \rightarrow F_1(0)} = C \left( \frac{E_L}{B_v} \right)^{-\alpha} e^{-\frac{\epsilon E_{L}}{\epsilon' \epsilon' \mu}}, \]

where \( C, \alpha, \) and \( \beta \) are fitting parameters. \( E_L \) is the energy of the state (Eq. (6)) with \( N = L \).

For the rate coefficients \( k_{q \rightarrow q'} \) of the endothermic transitions \( q \rightarrow q' \) where \( E_q < E_{q'} \), we apply the principle of detailed balancing,

\[ k_{q \rightarrow q'} = \frac{2J' + 1}{2J + 1} e^{-\frac{E_{q} - E_{q'}}{kBT}}, \]

Equations (6)–(11) provide a complete set of rate coefficients \( k_{qq'} \) for the NO A band. We used the same scaling law to calculate the rate coefficients \( k_{pp} \) for the NO X band, although strictly speaking this is not correct. NO X is a \( ^2\Pi \) state, while the ECS-EP law is only valid for \( ^2\Sigma^+ \) states. Since we are mostly interested in the RET of the NO A state, and RET of the NO X state is only included to refill the laser depleted state, this will have no significant effect on the calculated rotational population distributions of the NO A state.

5. De-excitation

In order to prevent the state density from accumulating in the reservoir state, we include a de-excitation process \( D_{rp} \) from the reservoir state to the ground state. The distribution of the species in the NO X state, originating from the reservoir state, is assumed not to disturb the equilibrium (they refill the X state assuming a Boltzmann distribution with rotational temperature equal to the gas temperature). The rate \( D_{rp} \) is given by

\[ D_{rp} = d \cdot f_p(T), \]

where \( d \) is a constant fit parameter. The exact value of \( d \) is not of significant influence on the model results, as long as it is chosen large enough such that no high density accumulates in the reservoir state. \( f_p \) is the population of state \( p \) according to the Boltzmann distribution,

\[ f_p(T) = \frac{(2J_p + 1)B_v}{k_BT} e^{-\frac{\epsilon E_p}{k_BT}}. \]
B. Simulation

To simulate the model we calculate, the total rate $K_{if}$ for the transition from initial state $i$ to final state $f$ (where $i$ and $f$ can be any state $p$, $q$, or $r$),

$$K_{if}(t) = B_{if} P(t) + A_{if} Q(t) + R_{if}.$$  \hfill (14)

All possible rates $K_{if}$ for the transitions $i \rightarrow f$ form a matrix $K_i$, as depicted in Figure 2. From this we can calculate a probability matrix $P(t)$ with the probabilities of a transition happening within a time step $dt$. The components $P_{if}$ are calculated assuming an exponential decay,

$$P_{if}(t) = 1 - e^{-K_{if}t} dt,$$  \hfill (15)

and the diagonals, representing no transition, are filled such that the total probability of any transition happening is 1,

$$P_{ii}(t) = 1 - \sum_{f \neq i} P_{if}(t).$$  \hfill (16)

The time step $dt$ is chosen small such that $P_{ii}(t)$ is close to 1 for each $i$, and the probability of a second transition within one time step is negligible.

The density $n_i$ of all the levels is represented by a row vector $n(t)$. The calculation of one time step can be performed by simply calculating the matrix product,

$$n(t + dt) = n(t) P(t).$$  \hfill (17)

C. Simulation results

1. RET rate coefficients

For the calculation of the RET rate coefficients we used the following values for the fitting parameters: $C = 1.6 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$, $\alpha = 0.2$, $\beta = 2.5$, and $\ell = 0.2$ nm. These values are chosen such that the rate coefficients correspond to experimental data by Lee et al.\textsuperscript{8} a comparison is shown in Figure 3. The coefficients are measured at 300 K with N$_2$ as buffer gas at 1 mbar pressure. For the calculation of the coefficients in Figure 3, we used the fine structure conserving transitions $F_1 \rightarrow F_1$ and $F_2 \rightarrow F_2$ in the ratio $F_1:F_2 = 5:1$. An indication for how the rate coefficients change for different species is given in Table I which shows that the rate coefficient for O$_2$ is slightly lower, and for He slightly higher. The mixture in our experiments is He with 3% air. Although in principle the fitting parameters depend on temperature and the species in the buffer gas, we assumed them to be constant (see also the discussion in Sec. IV).

Figure 4 shows the state-to-state RET rate coefficients of all $F_1$ transitions. The transitions $F_2 \rightarrow F_2$ and $F_2 \rightarrow F_1$ are not shown, but they are similar to $F_1 \rightarrow F_1$ and $F_1 \rightarrow F_2$, respectively. As to be expected, the RET rate decreases with increasing $N$. Note that especially at the higher states the transitions that change the fine structure are much slower than the transitions where the fine structure is conserved.
2. Thermalization at 300 K

We simulated the condition where all molecules are in the NO ground state when a very short (1 ps) laser pulse excites the $Q_{22} + Q_{12}(N = 14)$ transition at time $t = 0$. This means that the $F_1(14)$ and the $F_2(14)$ states are pumped instantly to a higher population, in a ratio $F_1:F_2 = 1.5$ (following the ratio of absorption coefficients). The gas temperature is set to $T = 300$ K. The time evolution of the rotational states is shown in Figure 5, and the population decay of the pumped states is shown in Figure 6.

The thermalization time is the time it takes for a distribution to become thermalized. In case of an extended pumping beam, we take $t = 0$ at the maximum laser intensity. Due to the asymptotic behavior of the thermalization process, the exact value of the thermalization time depends on the criterion of equilibrium. As threshold, we take—somewhat arbitrarily—1% of the population of the state, which has the highest population. We assume a distribution to be thermalized if the difference between the population $n_q$ and the Boltzmann distribution $f_q$ is less than this threshold for each rotational state $q$.

For 300 K the thermalization time is calculated to be 2.9 ns, as indicated in Figures 5 and 6. This is longer than the 0.5 ns mentioned by Lee et al., and can be attributed to fine structure changing transitions. Indeed from Figure 6, it can be seen that the combined population of the $F_1(14) + F_2(14)$ rotational state converges faster towards the Boltzmann distribution than the individual $F_1(14)$ and $F_2(14)$ states. This shows that in order to predict an accurate thermalization time, the fine structure splitting has to be taken into account.

More calculations of the thermalization time have been performed for different temperatures, each for a very short (1 ps) square laser profile, and for a measured laser profile (FWHM 3.8 ns) as shown in Figure 9. These simulation results are shown in Table II.

III. MEASUREMENTS OF THERMALIZATION TIME

A. Experimental setup

We measured the thermalization time of the rotational states of NO by laser induced fluorescence. The setup is described in detail in our previous work. As plasma source a coaxial microwave jet is used (see Hrycak et al.), with a gas flow of 6.0 slm He with 3% of dry air. The microwave power (forward minus reflected power) is 30 W.

The NO is excited from the NO $X(v = 0)$ to the NO $A(v = 0)$ band with a laser pulse around 224–227 nm. The laser beam is generated with a Sirah Cobra dye laser and an EdgeWave IS6III-E pump laser, and then frequency is doubled with a repetition rate of 4000 Hz. The laser wavelength is tunable such that we can excite individual rotational transitions. The fluorescence is detected from the NO $A(v = 0)$ to the NO $X(v = 2)$ band with a UV spectrometer around 242–248 nm. The spectrometer is a McPherson 234/302, attached to a Hamamatsu R8486 photomultiplier, which is connected via an amplifier to a computer with a Fast Comtec P7888 time digitizer card. The LIF setup is schematically drawn in Figure 7. The detection system has a maximum wavelength resolution of 0.1 nm, and a time resolution of 1 ns. This wavelength resolution means that we can...
measure the spectral shape of the vibrational emission band, but are unable to distinguish between individual rotational lines.

The high sensitivity of the system and the high repetition rate of the laser allow us to measure time and fluorescence wavelength resolved in one measurement. The measurements in this work are performed by setting the laser to a fixed wavelength while scanning the spectrometer along the vibrational band and measuring the time resolved spectrum. An example of such a measurement is shown in Figure 8. The image shows a constant spectrum due to plasma emission, with a superimposed spectrum due to the LIF signal as a result of a laser pulse at 224.877 nm. This wavelength allows to excite the \(Q_{21} + Q_{31}(N = 31)\) rotational transition. Time \(t = 0\) is defined at the maximum of the laser intensity.

### B. Time evolution of fluorescence spectrum

Figure 9 shows the decay of the LIF signal. It is obtained by integrating the measurement in Figure 8 over wavelength, and subtracting the constant plasma emission signal. The shape of the laser beam has been measured by setting the spectrometer to the laser wavelength and measuring the Rayleigh signal of ambient air. The laser beam has a FWHM of 3.8 ± 0.2 ns, but the shape is slightly asymmetric and the time at which the laser intensity has dropped to zero is 12 ± 1 ns, taken from the laser maximum.

For the integration of the full vibrational band, the signal increases during the laser pulse until the maximum intensity at \(t = 9\) ns, and decays exponentially after that. This indicates that the laser pumping is effective until \(t = 9\) ns and after that the laser is too weak to have an effect. For the integration of only a small wavelength band (which includes some lines of states directly pumped by the laser), the signal shows an initial decay, which is faster than exponentially. This is because of depopulation of the laser pumped states due to RET. After a few nanoseconds the decay follows the exponential decay of the full band. Note that this time is significantly longer than the duration of the laser pulse. The decay is fitted to obtain an exponential decay time \(\tau = 48.4 ± 0.4\) ns.

Figure 10 shows the fluorescence spectrum, obtained by integrating the measurement in Figure 8 for different time ranges, and subtracting the plasma emission signal. The spectra reflect the rotational distribution, which evolves towards a Boltzmann distribution. After approximately 40 ns, the rotational states are in equilibrium. The spectrum is fitted to obtain the rotational temperature \(T_{\text{rot}}\), as described in our previous work. The fitted temperature \(T_{\text{rot}} = 1479 ± 20\) K. The

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**FIG. 8.** Time and wavelength resolved fluorescence and emission signal of the NO \(A(v = 0) \rightarrow X(v = 2)\) transition inside the plasma at 2.0 mm axial position. At \(t = 0\) a laser pulse excites the \(Q_{21} + Q_{31}(N = 31)\) transition.

**FIG. 9.** Wavelength integrated LIF signal of the measurement shown in Figure 8, corrected for emission background. Note the difference in intensity (due to RET) during the first 30 ns.
error is the 95% confidence interval as obtained from the fitting routine.

We define $N_{\text{max}}$ as the most populated rotational state of the Boltzmann distribution. At $T_{\text{rot}} = 1479$ K, $N_{\text{max}} = 17$. The initial excitation by the laser is higher, at $N_{\text{pump}} = 31$. The RET is on average downward, which can be observed in the spectrum as a shifting towards higher wavelength.

Figure 11 shows LIF spectra similar to Figure 10, except the laser is tuned at 226.374 nm to pump the $Q_{21} + Q_{21}(31)$ transition. The pumped state is lower than $N_{\text{max}}$, which means that on average the RET is upward, and the spectrum shifts towards lower wavelengths.

C. Fitted temperature parameter

To obtain a rotational temperature from a rotational spectrum, a common method is a Boltzmann plot. If the rotational lines are only partially resolved, one has to use a fitting method such as the one described in Ref. 19. This method calculates the spectrum assuming a Boltzmann distribution of the rotational states, and finds the best fitting temperature parameter. If the rotational states are in equilibrium, this method works well and the temperature parameter can be interpreted as a kinetic temperature.

If the fitted spectrum is not in equilibrium, this is merely a fitting parameter which cannot be interpreted as a temperature. The fitting parameter is in fact the temperature parameter of the fitted Boltzmann distribution that can represent the actual rotational distribution best.

Unfortunately, it is not trivial to judge from a fit result whether the fitted temperature parameter is a real temperature or not. For example, in Figure 10, it is clear that the shapes of the spectra at 0–5 ns and 5–10 ns are not Boltzmann-like, and an attempted fit would not converge properly. But in Figure 11 the fitting of the spectra at 0–5 ns and 5–10 ns is reasonable, although the spectra are far from equilibrium. As is shown in the figure, the fitted parameter can deviate from the equilibrium gas temperature as much as 1000 K.

D. Thermalization time

We determined the time evolution of the fitted temperature parameter by fitting the fluorescence spectra at different times. The result is shown in Figure 12. The measurements of Figures 10 and 11 correspond to the lines 1 and 2. Similar time and wavelength resolved LIF measurements have been performed at different axial positions above the plasma (lines 3–6) and in a gas mixture with a premixed amount of NO at room temperature (lines 7 and 8). For each condition the laser was tuned to pump a high rotational state ($N_{\text{pump}} > N_{\text{max}}$) and a low rotational state ($N_{\text{pump}} < N_{\text{max}}$) compared to the rotational state which has the highest population at the given temperature, see Table II.

The results show that for each condition the high pumping state leads to an overestimation of the gas temperature in the first few nanoseconds, and the low pumping state leads to an underestimation of the gas temperature. After a certain thermalization time the fitted temperature parameter
converges to a constant rotational temperature $T_{\text{rot}}$, for which the actual rotational distribution is a Boltzmann distribution, independent of the pumped state. The thermalization time and $T_{\text{rot}}$ are shown in Table II. Note that the measurements which have the same $N_{\text{pump}}$, for example, 2 and 7 ($N_{\text{pump}} = 14$), or 4 and 6 ($N_{\text{pump}} = 6$), have similar initial values of the temperature parameter.

IV. DISCUSSION AND CONCLUSION

We have measured the thermalization time of rotational states of the NO $A$ ($v = 0$) band by following the evolution of the emission spectrum in time after excitation by a nanosecond laser pulse. The thermalization time was also simulated with a LIF-RET model. At room temperature the simulation and the experiments are consistent, the thermalization time is about the same ($11 \pm 1$ ns) as the duration of the laser pulse. Note that we cannot measure thermalization times shorter than the laser pulse duration. For room temperature the measured thermalization time must therefore be considered as an upper limit.

At higher temperatures the thermalization time increases, up to $35 \pm 4$ ns for $T = 1474$ K. This is significantly longer than the laser pulse duration, and of the same order as the state lifetime ($48.4 \pm 0.4$ ns). This means that in the measurements of the NO $A$ emission, at these temperatures, the effect of RET cannot be disregarded, and the time averaged rotational fluorescence spectrum of NO $A$ cannot be used as an indication of the gas temperature in plasma conditions as presented in this work.

The increasing thermalization times at elevated temperatures are not predicted in the simulation. The temperature influences the simulation of the thermalization time in a number of ways. With increasing temperature the density of collisional species decreases, causing a lower RET rate (Eq. (5)). Also, at higher temperatures the rotational population has to distribute over more states to achieve the Boltzmann equilibrium. Furthermore, the states have a larger $N$, which have smaller RET rates. These effects increase thermalization time, but are counteracted by the temperature dependence of the RET rate coefficients. The rate coefficients increase with temperature (Eqs. (9)–(11)), and therefore decrease the thermalization time. The simulations show that in total the thermalization time increases with temperature, but only slightly.

However, a temperature dependence of the fit parameters of the ECS-EP scaling law ($C$, $\alpha$, $\beta$, and $l_c$) is not taken into account. Most likely this unknown temperature dependence is the cause of the mismatch at higher temperatures between the thermalization times obtained from the simulation and the experiments, as indeed a temperature effect on the fitting parameters between 300–3000 K is found for OH in He.5 RET rate coefficients of NO at elevated temperatures and low pressure should be measured to be able to determine the temperature dependence of the ECS-EP scaling law. This is, however, outside the scope of this work.

Another consideration is the changing gas composition due to plasma induced chemistry. In the simulation only He is taken into account as collision partner, while in the experiments air is admixed to the He. The admixture of a few percent of air will most likely not significantly change the RET rates, since $N_2$ and $O_2$ have RET rate coefficients comparable to He (see Table I). In the plasma core the electron density is found to be a maximum of $7 \times 10^{18}$ m$^{-3}$, as measured by Thomson scattering.20 At this density RET due to electron impact will likely be negligible. The same holds for the ion densities which are expected to be of the same order, due to quasi-neutrality and expected low density of negative ions around 1500 K. The plasma is, however, found to produce significant amounts of radicals. For example, in the plasma core, the $O_2$ is found to be almost completely dissociated, with O densities up to $6 \times 10^{22}$ m$^{-3}$, as measured by two-photon absorption laser induced fluorescence.20 O and other radicals such as N are present in such quantities that they could potentially influence the RET rate, but their RET rate coefficients are not reported to our knowledge. The He itself is relatively inert and the He density does not significantly change in the plasma (apart from temperature effects). As a result, the radical species—which remain below a few percent of the gas density in the plasma—will only potentially increase the RET rate, not decrease (by more than a few percent). The observed increase in thermalization time cannot be explained by a change in the gas composition.

In our simulation we included the $F_1$ and $F_2$ fine structures. It is found that transitions where the fine structure is changed are much slower than the transitions where the fine structure is conserved. If the fine structure is not taken into account, measurements of state-to-state rate coefficients are mainly based on the fastest transitions ($F_1 \rightarrow F_1$ and $F_2 \rightarrow F_2$), while the thermalization time is mainly determined by the slowest transitions ($F_1 \leftrightarrow F_2$). This will lead to an underestimation of the thermalization time. It is therefore necessary to include the fine structure in calculations.

The results presented in this work explain why even at atmospheric pressure the NO $A$ rotational population distribution obtained by optical emission spectroscopy can be in non-equilibrium with the gas temperature and still reflect partially the nascent rotational population distribution. As NO $A$ is mainly important in plasmas at elevated temperatures, it shows the limitation of this band in the use of gas temperature determination.

14T. B. Settersten, B. D. Patterson, and W. H. Humphries, “Radiative lifetimes of NO A $^2S^+$ (v' = 0, 1, 2) and the electronic transition moment of the $A^2S^+\rightarrow X^2Π$ system,” J. Chem. Phys. 131(10), 104309 (2009).
21The excitation of a single rotational transition with a 1 ps laser pulse is merely a theoretical concept. An actual laser pulse with that length would have a bandwidth sufficient to excite several rotational transitions.
22Note that $\Delta N$ is used for the nomenclature of the branches, instead of $\Delta J$. 

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