STRATEGIES FOR NITRIC OXIDE LASER-INDUCED-FLUORESCENCE IN
HIGH-PRESSURE COMBUSTION SYSTEMS

TSD-165

Tonghun Lee

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Abstract

Practical diagnostic strategies for detection of temperature and nitric oxide (NO) in high pressure ($p$<60bar) combustion systems using Laser-Induced-Fluorescence (LIF) of nitric oxide are investigated. NO-LIF, when applied to elevated pressures, suffers from a decrease of signal due to pressure broadening and attenuation of the propagating laser beam/fluorescence signals. In addition, overlapping of neighboring excitation lines and interference from LIF of other species (mainly O$_2$ and CO$_2$) can significantly influence the overall signal. The main purpose of this study is to investigate NO-LIF strategies which minimize the impact of these complications or allow for correction of their effects. A comprehensive study of NO-LIF in a laboratory high-pressure flame was carried out for various flame stoichiometries, pressures and excitation wavelengths to develop optimized excitation and detection strategies for high-pressure applications. Four main issues are addressed in this study. First, optimized excitation strategies are investigated for high-pressure applications in the $A^2\Sigma^+-X^2\Pi$ (0,0), (0,1) and (0,2) bands of NO. Second, CO$_2$-LIF is identified as a major source of interference in the detection of NO-LIF in high-pressure combustion systems involving hydrocarbon chemistry. Third, an accurate multi-line thermometry technique for steady, high-pressure flames is proposed by fitting wavelength-scanned NO-LIF with computational simulations. Finally, measurements optimizing the detection strategies of 2-D NO-LIF imaging in high-pressure flames are reported. The discussion and demonstrations reported in this study provide a practical guideline for application of instantaneous 1-D or 2-D NO-LIF imaging in high-pressure combustion systems.
Acknowledgement

I came to Stanford in the summer of 2000 with a vision of applying diode lasers to semiconductor fabrication processes. During my first meeting with Professor Hanson, I was told that a new high-pressure combustion project was about to be launched and it would be a good opportunity for me to initiate myself to laser diagnostics. I wasn’t quite sure about a ‘transition project’, but once I got started, the unique challenges of building and operating a high-pressure burner and applying laser diagnostics generated a great interest in me. Near the end of summer, I knew that this project would be the one… and sure enough, it would eventually lead to a truly rewarding and exhilarating journey.

I am profoundly indebted to my advisor, Professor Ronald K. Hanson, for his guidance, encouragements and inspiration during my studies, particularly when things weren’t going at their best. I am privileged and proud to have been a part of his research group. I would also like to express my most sincere gratitude towards Dr. Jay Jeffries for leading and motivating me the whole way. His experience and vision empowered me to overcome many formidable challenges and I am most grateful.

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Thank you very much.
少年易老 學難成，
一寸光陰 不可輕，
未覺池塘 春草夢，
階前梧葉 已秋聲。

朱子 (1130-1200)

A boy ages easily and learning is hard to achieve,
A brief second lasts an eternity; do not judge it lightly,
The reeds by the pond have yet to wake from spring dreams,
Already, the leaves on the trees sound of fall.

Zhuzi (1130-1200)
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Chapter 1 Introduction

1.1 Background and Motivation

Since lasers were first introduced in the 1960s, laser spectroscopy has developed into an effective tool for fundamental research and applied diagnostics in nearly every major field of science and engineering. In particular, laser-based diagnostic methods have contributed greatly to fundamental combustion chemistry research and the development of practical combustion systems [1, 2]. The unique properties of laser light enable selective and quantitative probing of physical (e.g., pressure, temperature, flow-structure, gas-velocity, etc.) and chemical (e.g., species concentration, reaction kinetics, etc.) parameters with high temporal and spatial resolution. Unlike other probe-based techniques [3], laser spectroscopy offers a non-intrusive yet direct interrogation of the combustion process. Over the past few decades, innovations in laser technology and molecular spectroscopy have fueled the application of laser spectroscopy in the field of combustion. As a result, much of the research in modern combustion chemistry and modeling was built on experimental work made possible by spectroscopic methods. Currently, many laser-based optical methods are available for routine combustion diagnostics and studies are underway to optimize and refine their application range [2].

It is generally recognized that there is no single laser diagnostic strategy which is suited for all combustion conditions, and different strategies offer varying levels of accuracy, complexity and qualitative nature (single point, line or 2-D imaging) of obtainable data. In many practical combustors, the system constitutes a harsh, high-temperature, high-pressure environment with time-varying turbulent flow fields, multi-phase flows and generation of particulate matter. Therefore, for a given diagnostic method, practical combustion environments inherently offer unique challenges which complicate the application of the measurement method. Optimization and rigid testing of
Chapter 1

the spectroscopic strategy is required for each specific condition and controlled
experiments are used to improve the effectiveness of the strategy and to identify its
detection limits. The main spectroscopic method investigated in this study is laser-
induced fluorescence (LIF), which is a versatile and powerful tool for selective probing
of chemical species and capable of providing single point, 1-D spectrally-resolved and 2-
D spatially-resolved information.

The importance of combustion in our society and the ecological impact of
combustion byproducts is a major motivation for this work. Combustion is currently the
world’s dominant source of energy production and the foundation on which most of our
modern transportation system is based. The impact of combustion on the local and global
environment is well understood and is of grave concern to our generation [4, 5].
Emission of pollutants such as nitrogen oxides, sulfur oxides and particulate matter pose
severe health hazards and detrimental damage to the environment, and the effects of
carbon dioxide emission and subsequent greenhouse gas effects leading to global
warming are now common vocabulary in our everyday lives. With no clear alternative to
the present mass-produced combustion-based energy sources in sight, increasingly
stringent legislative restrictions are placed on combustion systems to mitigate the
harmful effects on our environment. Subsequently, these regulations drive new research
and technological innovations required for optimization of combustion efficiency and
reduction of pollutant emissions. In order to achieve this objective, computational and
experimental approaches, including laser spectroscopy, are used to understand the
complex chemistry and flow characteristics involved.

In the current study, LIF detection of nitric oxide (NO) is investigated in high-
pressures (1−60bar) flames, which reflect realistic conditions of practical combustors
(i.e., ic engines, gas turbines, etc.). NO is the primary nitrogen oxide emitted from most
combustion sources, and a major contributor in all nitrogen-oxide formation. Formation
chemistry of NO has been extensively studied and well documented in the literature [5, 6].

High-pressure combustion environments pose a unique set of challenges in the
application of NO-LIF, and these challenges constitute the major issue addressed in this
study. In this work, NO-LIF is investigated using excitation wavelengths in the $A−X$
bands, also known as the $\gamma$ bands. Optical diagnostics involving the $A-X$ systems are the most prevalent and routine method used for applications of NO-LIF, having reached a very high level of maturity over the last few decades. While many documented applications of NO-LIF in practical high-pressure combustion systems can be found in the literature, few strategies address the entire scope of complications caused by high-pressure effects in both excitation and detection of NO-LIF measurements. Many of these complications were first identified more than a decade ago [7-9], and various aspects have been continuously addressed over the years. The aim of this study is to conduct a comprehensive study of all the factors which require consideration in high-pressure NO-LIF and to propose and demonstrate a set of optimized excitation and detection strategies for detection of NO in practical combustion systems. Advances in computational NO-LIF simulations models, availability of a stable and well-characterized experimental apparatus for high-pressure combustion, enhanced understanding of NO spectroscopy and compilation of previous literature provide motivation and empower the researcher with the ability to conduct a comprehensive study of high-pressure NO-LIF.

1.2 Scope of Research

The aim of this study is to develop practical diagnostic strategies for detection of temperature and nitric oxide (NO) formation in high pressure ($p<60\text{bar}$) combustion systems using laser-induced-fluorescence (LIF) of nitric oxide. NO-LIF, when applied at elevated pressures, suffers from a decrease of signal due to pressure broadening, overlapping of the excitation lines, attenuation of the propagating laser beam/fluorescence signal and interference from other species (mainly $O_2$ and $CO_2$). A comprehensive study of NO-LIF in a laboratory high-pressure flame was carried out for various flame stoichiometries, pressures and excitation wavelengths to develop optimized strategies for application of NO-LIF in practical high-pressure combustion systems. Experiments are conducted at the High Temperature Gasdynamics Laboratory (HTGL) at Stanford University using a high-pressure laminar-flame burner. Four main issues are addressed in this study.
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First, optimized excitation strategies are investigated for high-pressure applications in the $A^2\Sigma^+ - X^2\Pi$ (0,0), (0,1) and (0,2) bands of NO. Performance of various excitation wavelengths are compared in order to provide guidelines for selecting an optimized strategy for a specific combustion condition. The comparison takes into account the influences of signal strength, laser and signal transmission, signal interference, and the pressure and temperature dependence of the LIF signal. Discussions are based on spectrally resolved 1-D line-imaging measurements in premixed methane/air flames at 1−60bar with equivalence ratios of $\phi=0.83−1.13$.

Second, absorption of UV light by carbon dioxide (CO$_2$) and subsequent emission of CO$_2$-LIF is identified as a major source of laser/fluorescence signal attenuation and detection interference, respectively. CO$_2$-LIF is investigated with excitation between 215 and 255nm with spectrally resolved 1-D line-imaging in 5−40bar premixed CH$_4$/O$_2$/Ar and CH$_4$/air flames. LIF of CO$_2$ consists of a broad (200−450nm) continuum with a faint superimposed structure. Implications of CO$_2$ absorption and LIF in the detection of NO are discussed. In addition, the signal from CO$_2$-LIF is found to be linear with pressure and laser fluence and potentially viable as an independent diagnostic tool for CO$_2$ detection; 2-D CO$_2$-LIF imaging using an optimized excitation strategy is demonstrated.

Third, an accurate temperature measurement technique for steady, high-pressure flames is proposed and demonstrated using excitation wavelength-scanned LIF with the NO $A^2\Sigma^+ - X^2\Pi$ (0,0) band. Excitation spectra are simulated with a computational spectral simulation program (LIFSim) and fit to the experimental data to extract gas temperatures. This “multi-line NO-LIF thermometry” is robust against elastic scattering and broadband LIF interference from other species, and yields absolute, calibration-free temperature measurements. It is an effective tool for studying high-pressure flame chemistry as well as providing a standard to evaluate and validate fast-imaging thermometry techniques for practical diagnostics of high-pressure combustion systems.

Finally, measurements to investigate the best detection wavelengths for 2-D NO-LIF imaging in high-pressure flames are reported. Design rules are presented to optimize the LIF detection wavelengths for quantitative NO-LIF measurements over a wide range of pressures (1−60bar) and temperatures. Simultaneous detection of LIF signals from multiple wavelength regions enables correction of the NO signal for interference from O$_2$.
and CO$_2$. In addition, spectrally resolved 1-D line imaging offers the possibility of highly selective detection of NO-LIF down to extremely low concentrations (<10ppm) using only a one-laser and one-camera setup. The discussion and demonstrations reported in this study provide a practical guideline for application of instantaneous 1-D or 2-D NO-LIF imaging in high-pressure combustion systems.

1.3 Thesis Overview

There are 8 chapters in this dissertation. Central to this thesis are four independent studies mentioned above; These topics are documented in chapters 4 to 7, respectively. Chapter 2 is a review of relevant molecular spectroscopy of NO and the basic principles of LIF and planar LIF (PLIF). A focus is placed on NO-LIF spectroscopy for high-pressure conditions and a literature survey of previous studies of high-pressure NO-LIF is reported. Computational simulations of NO-LIF and temperature fitting algorithms in this work are provided by LIFSim [10], and the underlying spectroscopy in the numerical simulation is presented. Chapter 3 reports on the experimental setup, data acquisition and processing used in this work. Technical details and experimental conditions are discussed. In chapter 4, optimized excitation strategies are investigated for high-pressure applications in the $A^2\Sigma^+ - X^2\Pi$ (0,0), (0,1) and (0,2) bands of NO. Problems caused by high-pressure environments in applying NO-LIF are discussed in depth. In chapter 5, absorption of UV light by CO$_2$ and subsequent emission of CO$_2$-LIF is identified as a major source for laser/fluorescence signal attenuation and detection interference. Chapter 6 introduces an accurate temperature measurement technique for steady, high-pressure flames using excitation wavelength-scanned LIF with the NO $A^2\Sigma^+ - X^2\Pi$ (0,0) band. Finally, practical 1-D and 2-D imaging strategies using NO-LIF in high-pressure flames are proposed and demonstrated in chapter 7. Conclusions are presented in chapter 8.
Chapter 1
Chapter 2 Spectroscopy

Laser-Induced Fluorescence (LIF) is a well-established and versatile tool for detection of chemical species in many disciplines of science. LIF is both species and quantum state selective, enabling measurements of concentration, temperature, pressure, density, velocities and reaction chemistry. In the field of combustion research, LIF has evolved into the most predominant method used for the measurement of minor species in flames and reacting flows. Planar LIF imaging (PLIF) has also matured into an effective tool for flow visualization and for imaging 2-D concentrations of chemical species and temperatures. The historical progress of LIF in the field of combustion and the broad range of applications can be found in several review articles [1, 11-13]. In this chapter, the basic theory of LIF spectroscopy required for interpretation of the LIF signal is discussed along with a survey of previous studies using NO-LIF as high-pressure combustion diagnostics. In addition, computational modeling of NO-LIF used in this work (LIFSim) is also documented.

2.1 Basic Theory of Laser Induced Fluorescence

2.1.1 LIF Modeling: Quasi-Two-Level System

A quasi-two-level LIF modeling approach is used to introduce the fundamental dynamics of LIF and relevant energy transfer processes involved. LIF can be viewed as a two-step process. First, target molecules are excited to higher energy states by absorption of resonant photons of the laser. Subsequently, molecules in the upper (excited) state relax back to the ground state by both radiative and non-radiative pathways. LIF signal results from radiative relaxation, where the excess energy is released in terms of fluorescent photons. Non-radiative relaxation pathways compete with LIF, and their
magnitude and impact are of great importance for quantitative interpretation of the signal. A simple schematic of a quasi-two-level model for LIF [14, 15] is shown in Figure 2-1 for a typical diatomic molecule with transitions occurring across two electronic energy states.

![Quasi-two-level system diagram](image)

*Figure 2-1* Quasi-two-level system with pertinent energy transfer processes. Rotational manifold for the $v'=1$ vibrational level is magnified in the inset.

The model consists of two electronic states ($A$ state: $1^{st}$ excited upper electronic state, $X$ state: ground electronic state), which are indicated by the two potential energy diagrams. Vibrational levels are shown with horizontal lines in each electronic state, and the rotational manifold attached to relevant $v'=1$ vibrational state are magnified in the right inset. The narrow spectral-width in modern lasers allows selective probing of individual rotational energy levels within the molecule. Once the molecule is excited to a
specific rovibrational energy level in the upper electronic state, it can migrate to neighboring energy levels or back down to the lower electronic state via several energy transfer pathways. The relevant energy transfer mechanisms are indicated with arrows and include absorption ($W_{12}$), stimulated emission ($W_{21}$), spontaneous emission ($A_{21}$), collisional quenching ($Q_{21}$) also known as electronic energy transfer, rotational energy transfer ($Q_{\text{RET}}$) and vibrational energy transfer ($Q_{\text{VET}}$). Dynamics of these energy transfer processes in diatomic molecules are further discussed below.

**Absorption ($W_{12}$), stimulated emission ($W_{21}$):** These are excitation and de-excitation mechanisms directly coupled with the laser/molecule interaction. Population in the ground state is initially excited to an upper state through absorption of the incident photons. Simultaneously, stimulated emission by the laser induces a reverse, deactivation process which causes the excited molecules in the upper state to relax down to the ground state. The absorption rate $W_{12}$ (s$^{-1}$) is linearly dependent on the Einstein $B_{12}$ coefficient (m$^3$/J·s$^2$) and can be represented as

$$W_{12} = \frac{B_{12}I_\nu}{c},$$  \hspace{1cm} (2.1)

where $I_\nu$ is the incident laser irradiance per unit frequency interval (spectral irradiance in units of W/cm$^2$·sec$^{-1}$) and $c$ is the speed of light. The stimulated emission rate $W_{21}$ (s$^{-1}$) is given in terms of the Einstein $B_{21}$ coefficient (m$^3$/J·s$^2$) as

$$W_{21} = \frac{B_{21}I_\nu}{c}. \hspace{1cm} (2.2)$$

Absorption and stimulated emission are coupled by the Einstein coefficients, which are related to each other as

$$g_1B_{12} = g_2B_{21}, \hspace{1cm} (2.3)$$
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where \( g_1 \) and \( g_2 \) are the degeneracies of states 1 and 2, respectively. Incident laser irradiance, \( I_\nu \), can also be written as a product of a normalized spectral irradiance \( I_\nu^* \) and a dimensionless overlap fraction, \( \Gamma \) [16] (rate of actual photon absorption rate to the monochromatic limit) in systems where transition and laser line shapes are spectrally broadened.

**Spontaneous emission (\( A_{21} \))**: The molecule is spontaneously relaxed from an excited upper state to other states \( i \) in the lower electronic state by emitting fluorescence. This radiative decay process constitutes the main mechanism for LIF signal production. The fluorescence rate is given by the Einstein \( A_{21} \) coefficient (s\(^{-1}\)), and the total fluorescence rate \( A \) is the sum of fluorescence rates over all individual transitions,

\[
A = \sum_i A_{2i}.
\]  

(2.4)

Spontaneous emission and stimulated emission are related by the Einstein coefficients,

\[
\frac{A_{21}}{B_{21}} = 8\pi\hbar\nu,
\]  

(2.5)

where \( \hbar \) is the Planck constant and \( \nu \) is the wavenumber of the individual transition.

**Rotational and vibrational energy transfer (\( Q_{RET} \) and \( Q_{VET} \))**: Molecules in specific rovibrational levels in the excited upper state can migrate to neighboring rotational or vibrational states by internal energy transfer processes during collision with other molecules. Rotational energy transfer (RET) is typically very fast and particularly important in LIF dynamics of short pulse nanosecond lasers. As the laser pumps population from specific rotational levels in the ground electronic state to those in the excited upper state, thermal equilibrium is perturbed. RET is responsible for refilling (or depleting) the relevant energy levels in an effort to re-establish thermally equilibrated
distributions. The rate of RET, $Q_{RET}$ (s$^{-1}$) induced by collisions with all other species $j$ in the system is given by

$$Q = \frac{p}{kT} \sum_j x_j v_j \sigma_{RET,j},$$  \hspace{1cm} (2.6)$$

where $x$ and $\nu$ are the mole fraction of species $j$ and relative velocity of the colliding particles ($\nu = \sqrt{8kT/\pi\mu}$ where $\mu$ is reduced mass, $\mu = m_1 m_2 / (m_1 + m_2)$), respectively. The parameter $\sigma$ (cm$^2$) is the effective rotational cross section for collisions with species $j$. Vibrational energy transfer (VET) is conceptually identical to RET, but for the fact that energy transfer occurs to neighboring vibrational levels. VET rates for NO are relatively slow in comparison to other energy transfer mechanisms, and the molecule will undergo relaxation to the ground electronic state before VET can occur.

**Quenching or electronic energy transfer ($Q_{21}$):** Molecules in the excited upper electronic state can relax down to a lower electronic energy state by collisions with other molecules. The overall rate of quenching $Q_{21}$ (s$^{-1}$) induced by collisions with all other species $j$ in the system is usually given in the same way as RET,

$$Q = \frac{p}{kT} \sum_j x_j v_j \sigma_{Q,j}.$$  \hspace{1cm} (2.7)$$

The term $\sigma$ is the quenching cross sections upon collision with the species $j$. Rotational and vibrational energy transfer maintain the molecule in the upper electronic state, thereby retaining the possibility of fluorescence. On the other hand, quenching forces the molecule back down to the lower electronic state. Quenching is therefore a directly competing process to LIF. It can also be seen from (2.7) that quenching is linearly dependent on pressure. Therefore, the impact of quenching becomes an important consideration particularly in high-pressure applications.
In addition to the energy transfer processes described above, other mechanisms can play significant roles in the analysis of LIF. Absorption of additional photons for molecules in the excited upper state can result in photoionization or photodissociation of the molecule. Excitation of the molecule into a rovibrational level of a bonding state above the dissociation energy or onto a potential surface crossing to an anti-bonding state can also result in dissociation of the molecule. This effect is known as predissociation. In other molecules, intersystem-crossing occurring between two overlapped potential surfaces can influence the dynamics of LIF. Additional details regarding molecular energy levels and laser spectroscopy can be found in the literature [1, 14, 15, 17].

2.1.2 LIF Equation: Two-Level Derivation

A two-level model is used to understand the basic physics of excitation and de-excitation processes involved in LIF. The LIF equation, which captures the key physics involved in the LIF process, can be derived from a non-transient analysis of the two level model.

The actual physics and distribution of energy levels of real diatomic molecules are more accurately described by a quantum-mechanical density-matrix approach [15, 18]. However, a non-transient rate-analysis is sufficient to reflect most of the basic concepts.
involved with the added benefit of mathematical simplicity. In theory, this type of simplified modeling is appropriate for atomic species and molecular systems with fully equilibrated or fully frozen rotational level manifolds. In practice, such models can be effectively used as a first approximation in actual LIF experiments. The basic transitions involved in the two-level model are shown in Figure 2-2. Absorption and stimulated emission rates are shown using $W_{12}$ and $W_{21}$, respectively. Quenching rates are shown as $Q_{21}$, and spontaneous emission rates are shown using $A_{21}$. The total number density is $n^0 = n_1 + n_2$, where $n_1$ and $n_2$ represent the population number density of states 1 and 2, respectively.

In a non-transient approach, we assume a constant laser intensity $I_{v}^0$ and therefore constant $W_{12}$ (eq. 2.1) and $W_{21}$ (eq. 2.2). Rate analysis can be performed to determine the rate of change of the population of molecules in level 2 as

$$\frac{dn_2}{dt} = n_2 = n_1 W_{12} - n_2 (W_{21} + Q_{21} + A_{21}).$$

(2.8)

At steady-state, $n_2 \approx 0$ and the population density of state 2 can be represented as

$$(n_2)_{\text{steady-state}} = n_1 \frac{W_{12}}{(W_{21} + Q_{21} + A_{21})}.$$

(2.9)

Two limits of operation can be envisioned using this type of steady state analysis. When laser energies are sufficiently high ($I_{v}^0 \geq I_{v}^{\text{sat}}$), absorption and stimulated emission balance and the population of the two energy states are determined by the ratio of the degeneracies in a two-level model: otherwise known as ‘saturation’. In this limit, the fluorescence signal is independent of laser intensity. The implications of this saturation effect, including benefits and disadvantages, will be further addressed in Section 2.1.4. The other mode of operation is ‘weak excitation’ ($I_{v}^0 \leq I_{v}^{\text{sat}}$), which occurs when the laser energy is below the threshold of saturation. When $I_{v}^0$ is sufficiently below $I_{v}^{\text{sat}}$, the
fluorescence signal is linearly proportional to laser intensity. Generally, this ‘linear LIF’ is preferred since laser non-uniformities and attenuation effects pose practical problems in applying LIF in the saturated regime. When the induced emission from level 2 is much weaker than the sum of collisional and spontaneous decay processes, i.e.,

\[ W_{21} = \frac{B_{21} I_v}{c} \ll A_{21} + Q_{21}, \]  

then \( n_2 \ll n_1 \), and \( n_1^0 \approx n_1 \). The population fraction in level 2 can be written as,

\[ n_2 = n_1^0 \frac{W_{12}}{A_{21} + Q_{21}}. \]  

As for a general description of the total LIF signal, it can be experimentally verified that the fluorescence signal is proportional to the population of level 2, the rate of spontaneous emission \( A_{21} \) and the solid angle of collection \( \Omega \). An expression for the fluorescence signal \( S_F \) can be written as,

\[ S_F = n_2 \times V \times A_{21} \times \frac{\Omega}{4\pi} \text{ (photons/s)}. \]  

In actual practice, the fluorescence signal is mostly quantified by using LIF intensity, \( I_{LIF} \) (W/m\(^2\)). The population density of level 2 (\( n_2 \)) also be replaced by a function of the initial ground state population (\( n_1^0 \)) using eq. 2.11. For more accurate modeling, we diverge from the strict concept of a two-level model and assume that the lower energy level has a manifold of rotational levels in thermal equilibrium. The population in these lower energy levels maintain a Boltzmann distribution [19] and the population of a specific rotational level can be written as \( n_1^0 \times f_B \), where \( f_B \) represents the Boltzmann fraction of the individual energy level. Based on these arguments, and by using eqs. 2.2, 2.11 and 2.12, the LIF intensity can be written as
\begin{equation}
I_{LIF} = c \times I_v^0 \times n_0^0 \times f_g \times B_{21} \times V \times \Gamma \times \frac{\Omega}{4\pi} \times \frac{A_{21}}{A_{21} + Q_{21}},
\end{equation}

where \( V \) is the volume of excited molecules, \( I_v^0 \) is the spectral intensity of the probing laser, \( c \) is the optical collection efficiency of the experimental setup and \( \Gamma \) is the dimensionless overlap function [16]. Equation 2.13 is known as the \textbf{LIF equation} and is the fundamental equation for interpretation of LIF signals in practical experimentation and non-transient computational simulations. The term \( A_{21}/A_{21} + Q_{21} \) in eq. 2.13 is called the fluorescence yield (\( \phi \)), which is the ratio of the spontaneous emission rate (LIF) to all excited state de-excitation rates. It is a direct representation of how much of the excited population will actually fluoresce. Values of \( A_{21} \) for nitric oxide \( A^2\Sigma^+ (\nu'=0) \) state are \( \sim 4.6 \times 10^6 \text{s}^{-1} \), quenching rates (\( Q_{21} \)) values are on the order of \( \sim 10^{10} \text{s}^{-1} \), and therefore, the fluorescence yield is on the order of \( \sim 10^{-4} \). For other molecules where predissociation and intersystem crossing are large, the fluorescence yield (\( \phi_{FL} \)) can be written as,

\begin{equation}
\phi_{FL} = \frac{A_{21}}{A_{21} + Q_{21} + P_{PD} + I_{IC}},
\end{equation}

where \( P_{PD} \) is the rate of predissocation and \( I_{IC} \) is the rate of intersystem crossing. Depending on the relative magnitudes of \( Q_{21}, P_{PD} \) and \( I_{IC} \), one term can be dominant in the denominator of the fluorescence yield and significantly impact the dynamics of LIF.

\subsection*{2.1.3 Broadening and Shifting of Spectral Lines}

Basic descriptions of mechanisms for broadening and shifting in lineshape functions are discussed in this section. These effects are especially pronounced in high-pressure applications and require attention. While the energy of a dipole transition is uniquely defined by the energy difference between two quantum states, actual transitions are not monochromatic and exhibit a certain spectral width and shape. These lineshape features depend on pressure, temperature, concentration and range of collision partners involved, and therefore play an important role in the interpretation of optical spectra.
Chapter 2

Lineshape functions $\phi(\nu)$ reflect the relative variation in the spectral absorption coefficient with frequency and have been defined so that its integral over frequency is unity,

$$\int_{-\infty}^{\infty} \phi(\nu) d\nu = 1. \quad (2.15)$$

The width of the lineshape is due to spectral broadening caused by phenomena in the medium that perturb the transition’s energy levels or the way in which individual atoms and molecules interact with light. There are three broadening mechanisms that contribute to the observed line width: natural broadening, Doppler broadening and collisional broadening. These broadening mechanisms are discussed in more detail below.

**Natural broadening**: Natural broadening is the spectral width exhibited by the molecule in the absence of interactions with other atoms. This is a result of the ‘Heisenberg Uncertainty Principle’, which states that energy and time cannot be simultaneously measured precisely. The uncertainty in the energy of level $i$ is this limited by

$$\Delta E_i \geq \frac{\hbar}{2\pi \tau_i}. \quad (2.16)$$

where $\tau_i$ is the uncertainty in time (i.e., lifetime) of level $i$. The lifetimes of the upper states, $\tau_i$, can be combined to give the total uncertainty of a transition. In units of frequency, this uncertainty is given by

$$\Delta v_N = \frac{1}{2\pi} \left( \sum_i \frac{1}{\tau_i} \right), \quad (2.17)$$

and the resulting lineshape function can be mathematically represented by a ‘Lorenztian function’. Since the uncertainty principle applies to all atoms in the same way, natural broadening is labeled as homogeneous. For most dipole transitions ($\tau \sim 10^{-100}$ns),
natural linewidths ($\Delta \nu_\lambda$) are in the order of $\sim 10^{-4}$–$10^{-3}$ cm$^{-1}$ and are much smaller than the linewidth resulting from either Doppler or pressure broadening at ambient conditions. Similarly, in the case of nitric oxide, natural broadening is negligible for most conditions.

**Doppler Broadening:** Doppler broadening is caused by the ‘Doppler Shift’ which occurs when a molecule has a velocity component in the same direction as the propagation of the laser beam. The velocity is a result of the thermal motion of the molecules and therefore directly dependent on temperature. Molecules are in constant motion and the distribution of their random velocities is dictated by the Maxwellian velocity distribution function. The Maxwellian velocity distribution tells us what fraction of the molecules is in each velocity class, each with its own Doppler shift. By calculating the shift for each velocity component and averaging over the distribution, we can determine the full width half max (FWHM, $\Delta \nu_D$) of a Doppler-broadened line,

$$
\Delta \nu_D = \nu_\sigma \left( \frac{8kT \ln 2}{mc^2} \right)^{1/2},
$$

where $\nu_\sigma$ (cm$^{-1}$) is the center wavelength of the line, $m$ the molecular mass, $k$ the Boltzmann constant and $c$ is the speed of light. Mathematically, the Doppler lineshape can be represented by a Gaussian function as

$$
\phi_D(\nu) = \frac{2}{\Delta \nu_D} \left( \frac{\ln 2}{\pi} \right)^{1/2} \exp \left\{ -4 \ln 2 \left( \frac{\nu - \nu_\sigma}{\Delta \nu_D} \right)^2 \right\}.
$$

Since the velocity of each individual molecule is different, Doppler broadening is also different for each molecule and is called inhomogeneous broadening with an inhomogeneous linewidth.

**Collisional Broadening:** Collisional broadening is caused by the interaction of atoms or molecules in a gas. The lifetime of an energy level is shortened due to perturbations that
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occur during the collision. As can be seen from (2.17), shortening of time constants $\tau$ leads to broadening of the spectral linewidths. Using an elastic collision model [19], the total collisional frequency of molecule $B$ with all other collisional partners can be written as

$$Z_B = P \sum_i X_i \pi \sigma_{ib}^2 \left( \frac{8kT}{\pi \mu_{ib}} \right)^{1/2},$$

(2.20)

where $P$ is pressure, $X_i$ is the mole fraction of species $i$, $\sigma_{ib}$ is the optical collision diameter between species $i$ and $B$, and $\mu_{ib}$ is the reduced mass ($\mu_{ib} = m_i m_B/(m_i + m_B)$). By using equation (2.17) with $1/\tau' = 1/\tau'' = Z_B$, the spectral width of collisional broadening ($\Delta \nu_C$) is given by,

$$\Delta \nu_C = \frac{Z_B}{\pi}.$$

(2.21)

In practice, it is extremely difficult to derive analytical expressions for the collisional widths due to the complexity of molecular interactions. Instead, empirical expressions with adjustable parameters derived from measurements are used [20]. Assuming that the interactions of different colliders $i$ are independent, the collisional broadening is modeled as a product of the system pressure and sum of the mole fraction for each perturber species $i$ multiplied with its process-dependent collisional halfwidth $2\gamma_{A-i}$ as,

$$\Delta \nu_C = P \sum_i X_i 2\gamma_{A-i}.$$

(2.22)

The broadening coefficient $2\gamma_{A-i}$ varies with temperature according to the following expression

$$2\gamma(T) = c 2\gamma(T_0) \left( \frac{T_0}{T} \right)^N,$$

(2.23)
To is the reference temperature, typically at 296 or 300K, and $N$ is the temperature coefficient (less than 1 and typically 0.5), and $c$ is an empirical scaling factor. For nitric oxide, parameters $2\gamma$, $c$ and $N$ were determined for the $A-X(0,0)$ transition by Chang, Dirosa and Hanson in shock tube experiments [20-22] and by Vyrodov et al. [23] for collisional partners Ar, He, N$_2$, H$_2$O, O$_2$ and NO. Collisional broadening leads to a lineshape that takes the form of a Lorentzian function and can be described as

$$\phi_c(\nu) = \frac{1}{2\pi} \frac{\Delta\nu_c}{(\nu - \nu_0)^2 + \left(\frac{\Delta\nu_c}{2}\right)^2},$$  \hspace{1cm} (2.24)

where $\nu_0$ is the center wavelength.

The combined effect of Doppler broadening and collisional broadening results in the convolution of two lineshape profiles, one with a Gaussian and the other a Lorentzian function. In cases where neither effect is negligible, Voigt profiles [24] are used to combine the effects of the two profiles, and are generally used to describe absorption lineshapes for diatomic molecules including nitric oxide. For high-pressure applications the dominant effect which influences the lineshape width is pressure broadening. Collisional broadening leads to a decrease in the peak intensity of the absorption features as well as a blending effect of neighboring transition lines. In addition to the increase in the spectral width, variation in temperature and pressure also induce shifting of the position of the line center as described below.

**Collisional Line Shifting (Pressure Shifting):** The collision of particles in a molecular system induces perturbation effects on the intermolecular potential of the molecules. Changes in the potential energy surface lead to differences in the energy level spacings, resulting in a shift of the center wavelength of the absorption lineshape. This effect is called pressure shifting or collisional shifting [25]. The empirical treatment of collisional shifting is analogous to that of collisional broadening and collisional shifting halfwidth, $\Delta\nu_S$ can be written as
\[ \Delta \nu_s = P \sum_i X_i \delta_{A-i} . \] (2.25)

where \( P \) is pressure, \( X_i \) is mole fraction of species \( i \) and \( \delta_{A,i} \) is the shift coefficient of species \( A \) with all other colliding species \( i \). The shift coefficient varies with temperature as

\[ \delta(T) = c \delta(T_o) \left( \frac{T_o}{T} \right)^M , \] (2.26)

where \( T_o \) is the reference temperature, \( M \) is the temperature coefficient and \( c \) is an empirical scaling factor. Empirical parameters \( \delta, c \) and \( M \) were measured for nitric oxide for varies colliders [20-23] for the \( A-X(0,0) \) transition in the literature.

**Figure 2-3** Excitation spectrum of nitric oxide at 1 and 20bar (numerical simulation using LIFSim) show pressure broadening and pressure shifting of spectral lines.
The combined effects of both pressure broadening and shifting are shown in Figure 2-3. As pressure is increased from 1 to 20 bar, there is significant broadening of the lineshape and a shift towards longer wavelengths. Accurate prediction of line broadening and shifting parameters is an important factor for quantitative analysis in the application of LIF.

2.1.4 Saturation and Population Recycling

Saturation effects in LIF and population recycling in multi-level models are introduced. In a simple two level model, saturation occurs when the induced emission is much larger than the collisional and spontaneous emission as

\[ W_{21} = \frac{B_{21} I_\nu}{\nu} \gg A_{21} + Q_{21}, \]  

(2.27)

in which case the fluorescence signal is independent of both the laser irradiance and the quenching rate [1, 26]. In the saturation regime, the rates of laser absorption and stimulated emission become so large that they dominate the state to state energy transfer into and out of the directly pumped levels. Since quenching does not influence the fluorescence intensity, LIF in the saturation regime can potentially be less complicated with the added benefit of maximizing the fluorescence yield and therefore increasing detection sensitivity. However, complete saturation is difficult to achieve due mainly to the specific wavelength region of the absorption or the magnitude of the saturation intensity. Furthermore, the decrease of energy in outer edges of the laser beam and the temporal deviation of pulse to pulse fluctuations introduce more complications. Therefore, application of LIF techniques in the linear regime using laser energy below the saturation is generally recommended and constitutes the basic approach in this thesis. As a criterion for saturation spectral irradiance \( I_\nu^{\text{sat}} \), the following expression can be derived using the two level analysis (ref [1]).
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\[ I_{\text{sat}} = \frac{(A_{21} + Q_{21})c}{B_{12} + B_{21}} \]  

(2.28)

where \( c \) is the speed of light. Saturation spectral irradiance, for most diatomic molecules can be attained by the use of high-power pulsed lasers with typical pulse durations less than 10ns. In the case of nitric oxide, a 1mJ @ 226nm (7ns) pulse focused into a 1mm diameter will start to show slight deviation from the linear regime.

For actual molecules with multiple energy levels (Figure 2-1), more complex dynamics regarding saturation should be considered. Saturation effects can occur by both an overfilling of the upper excited state or by depleting the lower ground state. Simultaneously, population can either be removed or added to the laser coupled states through rotational energy transfer (RET), which is on the same timescale as LIF and has important implications on the LIF dynamics. It has even more impact in high pressure conditions where the rapid increase in the rotational energy transfer refills the depleted ground state while removing excess population in the upper excited state, thereby greatly extending the linear regime of NO-LIF. This type of fast energy transfer and

Figure 2-4 Schematic of population recycling within a single laser pulse.
fluorescence mechanism can allow an excitation of the same molecule to occur multiple
times with the same laser pulse and is called population recycling.

A schematic of the population recycling is shown Figure 2-4. De-excited
population from the upper state is re-excited within the same laser pulse and is cycled
back to the upper excited energy level. A detailed modeling of these effects requires a
transient treatment with multiple energy levels and accurate determination of relevant
RET rates [27, 28].

2.1.5 LIF Temperature Dependence

LIF temperature dependence and sensitivity for practical thermometry
applications are discussed in this section. The temperature dependence of the LIF signal
occurs as a result of the temperature variation of the laser-excited ground state
population, the spectral overlap between the laser-spectral profile and the absorption
spectrum of the molecule, and the fluorescence yield as shown in eq. 2.13. As a result,
two practical implications can be considered. First, is the fact that quantitative analysis
using LIF requires knowledge of the local temperature to correct for the signal variation.
Second is that the LIF signal itself can be used for the detection of temperature in the
probe volume. Several strategies including both one-line and two-line wavelength
techniques have been developed to isolate the temperature sensitivity of the signal for
thermometry [29].

For PLIF imaging measurements, two-line thermometry techniques offer the
most versatility for the experimental effort and are dominantly used. Temperature is
obtained by using the ratio of fluorescence signals obtained from excitation of two
different ground states, where the absorbing state populations are assumed to follow
Boltzmann statistics and therefore are a function of temperature. Typically for nitric
oxide, rotational temperatures are obtained by selecting transitions that originate from
different rotational states within the same vibrational level of the electronic ground state.
The fluorescence ratio can be simplified and written as,
where subscripts 1 and 2 refer to transition 1 and 2, respectively. \( I_\nu^0 \) is the spectral irradiance of the laser, \( f_B \) is the Boltzmann distribution, \( B \) is the Einstein coefficient for stimulated absorption, \( \Gamma \) is the overlap function and \( \phi \) is the fluorescence yield \((A/A+Q)\). \( C_{12} \) is the experimental constant for differences in the optical efficiency. The main benefit of two-line thermometry is that by taking the ratio of fluorescence signals, the dependencies on the number density, mole fraction, overlap integral, partition function (for determination of Boltzmann fraction \([19]\)) and collisional quenching may be minimized. In practice, the fluorescence ratio can be written as an explicit function of temperature as,

\[
R_{12} = C_{12} \left( \frac{I_{\nu_1}^0 \times f_B(T) \times B_1 \times \Gamma_1(T) \times \phi_1(T)}{I_{\nu_2}^0 \times f_B(T) \times B_2 \times \Gamma_2(T) \times \phi_2(T)} \right),
\]

(2.29)

where \( \Delta \varepsilon_{12} \) is the energy difference (cm\(^{-1}\)) between the initial absorbing states. \( C_{12} \) can be calibrated from signal ratios using computational simulations or from a well characterized calibration source or region where temperature is accurately known.

Temperature sensitivity is a parameter of major concern when using LIF for detection of temperature. Generally, high sensitivity to temperature in the fluorescence ratio requires that the energy difference of the two absorbing states be comparable to or greater than the characteristic reaction temperature, i.e., \( \Delta \varepsilon_{12} \geq kT \). This sensitivity criterion is derived by differentiating eq. 2.30 as a function of temperature to obtain,

\[
\frac{dR_{12}}{dT} = \frac{[\Delta \varepsilon_{12} / kT]R_{12}}{T},
\]

(2.31)

Although eq. 2.31 indicates that maximizing \( \Delta \varepsilon_{12} \) is desirable, high rotational levels have small population which will decrease the signal-to-noise (SNR) of the
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detection system. By differentiating eq. 2.31 again (and setting to 0) with respect to \( \Delta \varepsilon_{12} \), the energy spacing which provides the maximum temperature sensitivity and subsequent temperature can be determined, \( T = \Delta \varepsilon_{12} / k \). In practice, a more revealing criterion for sensitivity can be measured by,

\[
\frac{dR_{12}}{dT} / R_{12} = \left[ \Delta \varepsilon_{12} / kT \right].
\] (2.32)

Temperature sensitivity as described by Eq. 2.32 takes into consideration the specific magnitude of the relevant temperature range by comparing the percentage of change in \( T \) and \( R_{12} \). Eq. 2.32 also indicates that maximizing \( \Delta \varepsilon_{12} \) is desirable to enhance the temperature sensitivity.

Selection of excitation lines which provide sensitivity in the temperature range of interest in an important step in applying LIF thermometry. It should be noted that high temperature sensitivity is not always considered a virtue. Quantitative imaging of species concentration in the absence of detailed temperature information can benefit from excitation lines which are insensitive to temperature. Two-line NO thermometry is used for imaging experiments in this study. In addition, a more refined and complex multi-fitting thermometry is introduced for accurate determination of temperature in high-pressure environments.

2.2 NO-LIF: Literature Survey

2.2.1 Benefits of using NO as a LIF Tracer

Using NO as a primary tracer for LIF measurements offers a number of advantages from a diagnostic standpoint. First and foremost, NO has a relatively strong absorption cross-section and good fluorescence efficiency, resulting in strong LIF signals for detection. Second, there is strong nonresonant fluorescence signal, which when combined with spectral filtering can provide detection strategies free from radiative trapping or Rayleigh scattering. Third, NO does not exhibit \( J \)-dependent (rotational-level
dependent) radiative lifetimes or quenching rates that can lead to systematic measurement errors. Fourth, NO is a molecule whose spectroscopy is well characterized. This facilitates numerical modeling of the LIF signal, which has reached a high level of maturity and is able to provide flexibility in the design and interpretation of NO-LIF experiments. As a LIF tracer, NO is relative stable in harsh combustion environments (i.e., high temperatures \(T \geq 2000\text{K}\) and pressures \(P \geq 30\text{bar}\)). Finally, NO can be easily seeded to combustors for making temperature measurements throughout the entire flowfield. This is in contrast to molecules such as OH, which are only feasible in the reaction zones or burned gas regions.

### 2.2.2 NO-LIF in the Literature

There is an extensive collection of literature regarding NO-LIF for both laboratory and practical combustor applications. One of the first uses of NO-LIF was reported by Grieser and Barnes [30], in which single-point NO fluorescence measurements were used to measure concentrations in a flame. McKenzie and Gross [31] later suggested the use of two-photon LIF of NO for single-point thermometry. The first 2-D imaging of NO fluorescence was reported by Kychakoff \textit{et al.} [32], where seeded NO was visualized in CH\(_4\)/air flames. Kychakoff suggested the use of 2-D imaging for temperature measurements without reporting experimental data in this publication. The first instantaneous 2-D PLIF temperature imaging was reported by Seitzman \textit{et al.} [33], using a one-line technique to measure the rotational temperature of NO seeded in fuel lean methane-air flames. Two-line PLIF temperature imaging measurements were first reported by Paul \textit{et al.} [34]. These citations represent only a fraction of the NO-LIF applications in the literature, so chosen for their pioneering contribution. Relevant to this study, a large number of NO-LIF measurements have been performed in high-pressure flames using both \(D-X\) and \(A-X\) strategies. The following discussion focuses on high-pressure applications of NO-LIF, although some atmospheric pressure work is cited where appropriate.

#### \(D-X(0,1)\) excitation overview
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The NO $D-X(0,1)$ system at 192–195nm has the benefit that it can be probed with 193nm radiation from an ArF excimer laser [35, 36]. Andresen et al. [37] utilized the NO $D-X(0,1)$ transition for qualitative NO-LIF imaging in a spark-ignition gasoline engine with iso-octane. Arnold et al. [38] carried out measurements in a direct-injection Diesel engine fueled using n-heptane as fuel. NO imaging in a prechamber-injected Diesel engine with n-heptane and Diesel fuel was reported by ter Meulen et al. [39, 40]. They subsequently performed measurements in a direct-injection Diesel engine with maximum pressures of 75bar [41, 42]. Tanaka et al. performed measurements qualitative measurements using the $D-X(0,1)$ transition in a spark-ignition engine [43]. Most of the work note above used excitation of the $D-X(0,1)$ $R_1(26.5) + Q_1(32.5)$ transition by tuning an ArF excimer laser to 193.38nm, due to the minimized interference from O$_2$ interference at this wavelength [44].

The major disadvantage of using the NO $D-X(0,1)$ transition is the severe attenuation of the short-wavelength laser beam and signal light in the high-pressure combustion environment. This commonly leads to complete signal loss at portions in the engine cycle, making quantitative interpretation of the signal impossible. Techniques applied for correction of the attenuation in the literature are based on many uncertain assumptions [39]. Interpretation of the LIF signal is further complicated by the fact that knowledge regarding quenching and energy transfer processes occurring in the NO D state is not well-known. Attempts to quantify LIF signals [41, 42] must rely on unverified assumptions about the dependence of fluorescence quantum yield on pressure and temperature.

$A-X(0,0)$ excitation overview

The $A-X(0,0)$ transitions at 224–227nm are the transitions most frequently used by past workers. This has evolved into the standard technique for NO detection in flames, and is the only technique sensitive to cold NO, e.g., in flowfield diagnostics [45, 46]. High-pressure applications include small-scale laboratory flames as well as gasoline and Diesel internal combustion engines.

A large number of NO measurements have been reported in high-pressure laboratory burners. Laurendeau and co-workers have extensively studied NO formation...
in premixed, partially premixed, and non-premixed flames. They have reported quantitative single-point NO measurements in ethane/air flames up to 15bar [47-50], ethylene/air flames up to 12bar [51], methane/air flames up to 15bar [52], heptane spray flames at 2–5bar [53-55], and CO/H<sub>2</sub>/CH<sub>4</sub>/air flames at 1–12bar [56]. Most of the measurements were carried out using a frequency-doubled dye laser system tuned to the Q<sub>2</sub>(26.5) transition at 225.58nm to minimize temperature dependence of the ground state population. Spectroscopic measurements in the 1–12bar range were carried out to investigate the O<sub>2</sub> LIF interference [16, 57], and the influence of pressure of the calibration was investigated [58]. Narrowband monochromator detection (<5nm bandpass) was used for most of the experiments for suppression of interference signals, with increased interference being confirmed with broadband detection in an imaging configuration [54, 59]. The first measurements made in high-pressure flames exceeding 20bar were made by Vyrodov and co-workers. The have reported measurements in a steady-state laminar flame burner up to 60bar [7], and are the first to apply a multi-line fitting thermometry technique using a detailed spectral simulation model. Vyrodov et al. have also contributed to the database of collisional broadening coefficients of NO with N<sub>2</sub> and Ar as colliders in high-pressure environments [23]. DiRosa and co-workers have reported high-pressure NO-LIF spectroscopy in flames up to 10bar [8], and presented a numerical simulation model for both NO and O<sub>2</sub> LIF. As a result optimal transitions to suppress the interference from O<sub>2</sub> LIF were suggested. In addition, DiRosa et al. reported collisional broadening and shifting parameters for NO in high-pressure combustion environments [20, 21]. These pioneering studies in high-pressure NO-LIF identified many of the problems which are addressed in this thesis.

For practical PLIF applications using the A–X(0,0) band, Alatas et al. [60] performed the first in-cylinder measurements. No details regarding specific excitation or detection bandpass was given. Bräumer et al. used the R<sub>1</sub>+Q<sub>21</sub>(21.5) transition at 225.25nm for quantitative in-cylinder NO number density measurements in a spark-ignition engine fueled with propane [61]. 248nm output from a tunable KrF excimer laser was shifted to 226nm using a 10bar hydrogen cell (Raman shifter). Dec and Canaan [62] performed imaging measurements in a direct-injection Diesel engine fueled with low-sooting Diesel fuel, presenting semi-quantitative in-cylinder NO
concentrations throughout the combustion cycle with pressures up to 65 bar. A frequency-doubled OPO system was used to excite the $P_1(23.5)$, $Q_1+P_{21}(14.5)$, $Q_2+R_{12}(20.5)$ feature at 226.03 nm. This transition was proposed by Battles and Hanson [63] based on detailed spectroscopic investigations in flames up to 10 bar by DiRosa et al. [8]. Van den Boom et al. used the same transition in a direct-injected Diesel engine fueled with commercial Diesel [64]. Nakagawa et al. have used 226.26 nm excitation in Diesel spray flames in a modified single-cylinder engine [65].

The $A−X(0,0)$ transition at 226 nm also suffers from strong attenuation in engines, making measurements impossible at crank angles near the top dead center. In our studies reported later in the thesis, we observed an attenuation of around ~40% across an 8 mm region at 60 bar. This absorption is of concern and also motivation to investigate excitation in longer-wavelength vibrational bands.

**$A−X(0,1)$ excitation overview**

Application of NO $A−X(0,1)$ excitation in the 233–237 nm wavelength range is promising because it reduces laser beam attenuation while still providing sufficiently strong signals. Furthermore, optical parametric oscillator systems (OPOs) provide high laser pulse energies throughout the UV (up to 30 mJ/pulse) needed for imaging measurements.

To our knowledge, the first application of NO $A−X(0,1)$ LIF in high-pressure combustion was performed by Jamette et al. in a direct-injection spark-ignition gasoline engine [66]. The authors used the $R_{1}+Q_{21}(22.5)$, $Q_1+P_{21}(8.5)$, $Q_2+R_{12}(17.5)$ feature at 236.22 nm based on simulations of LIF excitation spectra of NO and $O_2$ in order to maximize the NO/$O_2$ LIF ratio. Laser beam attenuation also motivated Chou et al. to use $A−X(0,1)$ for LIF measurements in an atmospheric-pressure $NH_3/O_2$ flame to avoid quasi-continuum $NH_3$ absorption near 226 nm [67]. Similar strategies have been reported in low pressure LIF measurements [68] and cavity ring-down investigations [69].

**$A−X(0,2)$ excitation overview**

The choice of $A−X(0,2)$ excitation at 244–247 nm has the benefit of enabling use of a KrF excimer laser to excite the $O_{12}$ bandhead at 247.94 nm. This high-power accessibility
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is offset by the low populations in the \( \nu' = 2 \) vibrational level. This approach was first proposed by Schulz et al. to avoid the strong laser and signal attenuation observed with \( D - X(0,1) \) or \( A - X(0,0) \) excitation [70]. They performed detailed spectroscopic investigations in premixed flat methane/air flames up to 40bar to assess interference from \( \mathrm{O}_2 \) LIF, and reported that the NO \( A - X(0,2) \) \( \mathrm{O}_{12} \) bandhead coincides with a local minimum in the \( \mathrm{O}_2 B - X \) band. In addition \( (0,2) \) excitation offers the possibility of blue-shifted detection of the \((0,0)\) and \((0,1)\) emission, providing an important advantage by eliminating the detection of \( \mathrm{CO}_2 \) and PAH LIF. This scheme was also investigated in sooting high-pressure ethylene/air flames [71], where strong PAH fluorescence is observed red-shifted to the excitation wavelength but the blue-shifted NO detection minimizes this interference. Schulz and co-workers applied this scheme for quantitative NO concentration imaging in a spark-ignition engine fueled with propane [72]. Simultaneous Rayleigh temperature measurements were performed and used to quantify the NO LIF images. Quantitative imaging measurements were also performed in spark-ignition engines fueled with iso-octane running under premixed [73] and non-premixed (direct-injected) conditions [74, 75], and in direct-injected Diesel engines fueled with commercial Diesel fuel [76, 77]. Andresen and co-workers performed spectroscopic investigations on NO LIF with \( A - X(0,2) \) excitation in an atmospheric-pressure flame, measured transmission properties in a spark-ignition engine fueled with iso-octane, and showed qualitative NO-LIF distributions [78, 79]. Quantitative one-dimensional measurements were shown in a spark-ignition engine fueled with iso-octane and regular gasoline [80]. Qualitative in-cylinder measurements using \( A - X(0,2) \) bandhead excitation have been performed by Akihama et al. in a port-fuel injected spark-ignition engine fueled with iso-octane at pressures up to 15bar [81]. Recently, NO concentration measurements have been made in a direct-stratified-injection gasoline engine by Bessler et al. [82].

2.3 Computational Simulation of NO-LIF: LIFSim

The simulation code, LIFSim [10], which is extensively used in this study for modeling NO-LIF, is briefly introduced in this section. The LIF model and spectroscopy
data used in LIFSim are compiled in order to provide a scope of the numerical simulations which compliment the experimental work in this thesis. There are several basic criteria which must be satisfied to perform quantitative LIF measurements for a given molecule. First, an understanding of the absorption spectrum along with practical accessibility with a tunable laser is required. Second, the emission spectrum of the molecule should be well known. Third, the rate of radiative decay of the excited state should be known, due to the fact that fluorescence power is proportional to this rate. Fourth, an understanding of non-radiative pathways including quenching, photoionization and/or predissociation should be known. For the work in this thesis, most of the aforementioned requirements are provided by utilizing a computational simulation of nitric oxide (LIFSim). LIFSim was developed by Wolfgang Bessler (2003, Heidelberg University), and is based on a previous simulation code by Volker Sick (1995, Heidelberg University and later University of Michigan). It is available in both a DOS shell executable format (programmed using C++) or via an interactive web interface (www.lifsim.com). The discussions in this section are based on recent publication by Bessler et al. [10].

2.3.1 Other NO-LIF Modeling Simulations

Spectroscopic simulation programs for NO have been proposed in several formats, each with varying degrees of complexity in the description of the LIF dynamics. LIFBASE by Luque and Crosley (SRI International) is the most general and widely distributed program [83]. Apart from NO, LIFBASE implements the spectroscopy of several diatomics (OH, OD, NO, CH, CN, N₂, SiH and CH); note that O₂ is not included. While LIFBASE has a broad application base, spectroscopic details are incomplete for many of the molecules including nitric oxide, such as the lack of a full quenching model.

NO and OH spectroscopic models and fitting functions were implemented in a simulation program by Vyrodov and Heinze [23]. This model also lacked a detailed quenching model. Initial application of multi-line thermometry in high-pressure flames was demonstrated with this model, though successful temperature detection was reported for flames under 20bar.
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An advanced simulation program for NO and O$_2$ was developed by DiRosa (Stanford University) [8] in Fortran, and used for pioneering work in NO-LIF. Details of spectroscopic parameters implemented in the modeling were similar to LIFSim. The ability to model O$_2$ simultaneously provided the ability to optimize excitation lines for UV NO-LIF in the presence of interference from O$_2$-LIF.

All the above models apply steady-state LIF models, where the population of the laser-coupled ground state is considered to be in equilibrium and rapid RET is assumed. Most requirements of experimental applications using NO-LIF can be met with a steady state model. For transient modeling of NO excitation dynamics, a time-resolved simulation model has been implemented by Daily (University of Colorado) [27]. This model currently includes multiple energy levels (950) in the A–X absorption and emission branches and solving for the individual rate equations for all the involved quantum states. This type of model clearly shows the effects of fast RET and relatively slow VET (negligible) which can result in population recycling effects as mentioned in Section 2.1.4.

2.3.2 LIFSim: Functionality

The aim of LIFSim is to enable computational simulations of excitation and emission processes in LIF (NO and O$_2$) to assist in the quantitative analysis of species concentration and temperature detection in practical experiments. A brief description of the functions offered by LIFSim is listed below.

*Calculation of absorption spectra* – The laser is tuned over a certain wavelength range and the absorption spectra are recorded. Parameters for calculation are temperature, pressure, excitation wavelength range, spectral resolution, species concentration, laser parameters and the molecular spectroscopy parameters (excluding quenching).

*Calculation of LIF excitation spectra* – The laser is tuned over a certain wavelength range and the LIF signal is recorded at each spectral position. Parameters for calculation are temperature, pressure, excitation wavelength range, spectral resolution. The detection bandpass can be set arbitrarily.
Calculation of LIF fluorescence emission spectra – The laser is set to a fixed excitation wavelength, and spectrally resolved LIF emission spectra are recorded. Parameters for calculation are temperature, pressure, excitation wavelength, wavelength range and resolution for the fluorescence spectrum, and simulated monochromator function (slit function) with Gaussian and Lorenztian contribution.

Pressure and Temperature dependence of LIF signals – The LIF signal is calculated for a range of pressures and temperatures. Parameters for calculation are temperature range and resolution, pressure range and resolution and excitation wavelength. Calculations can be performed on a per molecule or per-volume basis.

Fit of simulated LIF excitation spectra to experimental data – Experimental LIF excitation spectra can be fit using simulation by varying input parameters. The fitting is done via nonlinear-least-square-fitting (Levenberg-Marquadt) [84]. A modified application of this code is shown later in Chapter.6.

![Three-level LIF model in LIFSimg](image)

*Figure 2-5* Three-level LIF model in LIFSimg. $W_{12}$ and $W_{21}$ are absorption and emission, respectively. $A_{21}$ and $A_{31}$ are spontaneous emission. $Q_{21}$ is quenching and $P$ is predissociation. $R_{13}$ and $R_{31}$ show rotational energy transfer.

2.3.3 LIFSimg: LIF Model

A simple non-transient three-level LIF model is used for the calculation of LIF signals in LIFSimg. The three levels are the lower ground level, upper excited level and a
rotational manifold attached to the ground level. An energy level diagram of this model is shown in Figure 2-5.

The simplicity of the model enables rapid calculations of the LIF signals while the three-level concept is sufficient to capture most of the relevant physics required for analysis of experimental data. The model assumes an equilibrium population of the laser-coupled ground state (i.e., rapid ground state RET is assumed). A single laser-coupled upper state is used with no excited-state energy transfer. Fluorescence emission is calculated from a single upper state within the allowed branches to all possible rotational and vibrational levels of the electronic ground state, with quenching and predissociation (for O₂) as the only non-radiative depopulation mechanism of the excited upper state. The steady-state rate equation approach in the linear regime for a three-level model collapses to a form identical to the LIF equation (eq. 2.13), which forms the backbone of the calculation.

In high-pressure applications, collisional-broadening and line-overlap severely impact the analysis of data, and a simulation tool which can accurately reflect these phenomena is required. The accuracy of the model is dependent on the spectroscopic parameters which are used in the calculations. The molecule specific parameters used in LIFSIm are as follows:

**Term energies (calculation of ground state populations and partition function):** Term energies are calculated using expressions of Paul [85]. These expressions use the Hamiltonians of Amiot et al. [86], following the work of Zare et al. [87]. The constants were taken from Coudert et al. [88] and Amiot et al. [89].

**Transition energy (line positions) and partition function:** From the term energies, the transition energies of the NO A−X system are calculated using the selection rules of ²Σ−²Π dipole transitions. The Partition function is also calculated from the term energies by fitting polynomial expressions as a function of temperature.

**Transition strengths (absorption and emission intensities):** The calculations of transition strengths and vibrational oscillator strengths are taken from Laux and Kruger [90]: these values are based on ab initio calculations and potential energy curves obtained with recent spectroscopic constants.
**Parameters for O\textsubscript{2} B–X:** Term values and Einstein coefficients are calculated using expressions by Sick and Szabadi [91]. Predissociation line widths are taken from Lewis *et al.* [92]. Collisional broadening widths are taken from Lewis *et al.* [93] and Sick *et al.* [94]. Quenching is neglected.

**Collisional line broadening and shifting parameters:** Collisional line broadening and shifting for NO A–X transitions were taken from measurements made by Chang, DiRosa and Hanson [20-22] for H\textsubscript{2}O, O\textsubscript{2}, Ar, N\textsubscript{2} and NO at room temperatures in a static cell.

**Quenching cross sections:** For calculation of quenching rates, the “harpoon” quenching model from Paul *et al.* [95] is used. Parameters used in the modeling are taken directly from the literature [96, 97].
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Chapter 3 Experimental Facility and Procedure

In this chapter, details regarding the experimental facility as well as a schematic of the computational framework for data acquisition and processing are discussed. The experimental work included in this thesis was performed at the High Temperature Gas Dynamics laboratory (HTGL) at Stanford University. A high-pressure combustion diagnostics lab was assembled in the HTGL and has been in operation since 2000 to facilitate laser diagnostics research in practical high-pressure combustion environments, and served as the primary location for the experimental work presented in this thesis. The focal point of the experimental setup in the high-pressure combustion lab is a steady, laminar, high-pressure flat-flame burner with four-way optical access, providing well-characterized high-pressure flames over a wide range of pressures and equivalence ratios. Investigation of various laser excitation/detection strategies were enabled by additionally employing high-power lasers, optics, intensified cameras, spectrometers and data acquisition systems.

3.1 Facility Overview

3.1.1 High-Pressure Burner

The original design of the high-pressure burner was proposed and demonstrated by Eberius et al. at the Deutsches Zentrum für Luft- und Raumfahrt (DLR) in Stuttgart, Germany [98]. Laminar, premixed methane/air flat flames at pressures from 1 to 60bar are stabilized on a porous sintered stainless-steel matrix of 8mm in diameter. Figure 3-1 shows a photograph of the outside housing of the burner (left), and a photo of the flame at 10bar through one of the optical access windows (right). The flame itself is flat and
Chapter 3

shown as a bright horizontal line in the window. The cone on the top of the flame is due to the chemiluminescence from the post combustion gases.

![Figure 3-1](image)

**Figure 3-1** The high-pressure burner at Stanford University. Burner housing with optical access windows (left) and a $\phi=0.9$, CH$_4$/air flame at 10bar (right).

Burner specifications, including operation and control systems, are discussed in detail below. The references made to individual components attached to the burner are shown in Figure 3-2.

**Burner housing:** The burner housing is made from stainless steel and the inner diameter of the combustion chamber is 60mm. The upper housing can be detached and lifted up to reveal the burner matrix as shown in Figure 3-2. The entire housing is mounted on a translational stage (Velmex) for freedom of movement in the vertical direction. This provides the ability to probe the flame at different heights without changing the alignment of the laser and detection system.

**Optical access:** Optical access to the flame was possible via four quartz windows (Heraeus, Suprasil 2 Grade) on the upper housing of the burner. The windows are 35mm in diameter and 15mm thick. The edges of the windows have a 2mm (15° to the sidewall)
Experimental Facility and Procedure

bevel on either side to avoid stress concentration from the force exerted by the pressurized gases inside the chamber.

Figure 3-2 Schematic of the high-pressure burner. The upper housing of the burner is detached to reveal the burner matrix.

The window is secured with a Viton O-ring (2mm diameter) around the circumference, and pressed on either side by two flat Teflon rings for sealing. A schematic of the optical
access window, Teflon ring and fitting are shown in Figure 3-3. As shown in the figure, the window is pushed into the burner housing by an outside flange. It should be noted that once the window is fastened into the burner, there is no adequate way to pull it out except by slowly pushing it out with high-pressure air from the inside. This procedure is difficult and can easily lead to cracking in the edges of the window. Design of a more efficient housing should enable the entire window assembly to be detached for cleaning.

![Figure 3-3 Optical access window dimensions and fitting assembly.](image)

**Preheating and Cooling:** The upper housing is cooled by a circulation of silicon oil (Lauda Ecoline 006 tub, with a Lauda E300-control unit) operated at 75°C. The oil circulator is used for preheating the burner before the ignition. During operation, the oil serves a dual purpose as a coolant to prevent overheating of the housing. Preheating the chamber before ignition is important, as it helps to prevent condensation on the windows, which can potentially lead to sticking and baking of particles to the quartz surface. Preheating is also achieved by heating coils around the base of the lower chamber. A current is passed through heating coils surrounding the base of the lower housing, and is feedback controlled via a temperature controller (Red Lion, T48) to a setting of 100°C. An R-type thermocouple embedded in the block of the lower chamber provides the
temperature information for the control unit. Preheating the entire burner prior to ignition requires about 20 minutes.

![Image](image.png)

**Figure 3-4** Lower housing of the burner. Flame is stabilized on the center cone.

**Flame Stabilization**: The flame is a flat circular flame stabilized on a porous stainless steel matrix (Tridelta, R10) which is 8mm in diameter and 8mm thick. It is fixed into a copper cone, and the entire assembly is fixed onto a shaft protruding from the lower housing chamber. A photograph of the matrix including the lower portion of the burner is shown in Figure 3-4. The sintered matrix comes as a plate and is machined and inserted into a copper matrix cone. During this process of inserting the matrix into the cone, the copper cone must be expanded by heat and cooled to clasp lightly around the matrix. Forcing the matrix into the cone will crush the pores and hinder the flow of gases at high-pressures or lead to irregular flame patterns. Stabilization of the flame occurs when the local flame speeds match the local flow velocity [5, 99]. In the high-pressure burner, flame speed is controlled by removal of energy and radicals on the burner matrix in addition to the stabilization effects of the coflow air. The fresh gases are preheated to 100°C by heating coils embedded around the stand of the matrix cone to maintain a
controlled temperature of the pre-ignition gas. Temperature is feedback controlled as the preheating coils described above. For this, an additional R-type thermocouple is embedded under the burner matrix assembly.

**Pressure Regulation**: The high pressure inside the chamber is mainly created by the co-flow of compressed air around the burner matrix. The operation range of the burner is from 1 to 60bar for the current study, though the chamber is designed for a maximum operating pressure of ~200bar. The flow is choked at the exhaust-end using a combination of a main switch valve (Swagelok ball valve) and an additional motored needle valve unit (Gulex N802/0/20U/12s/E). The main valve is open only for atmospheric pressure flames and fully closed for all high-pressure flames (>1bar). The needle valve unit is primarily used for fine control of pressure at pressures above 1bar. The tolerance for pressure stabilization is ±0.1bar, and is monitored via a piezoelectric pressure transducer (Kistler 4293A50: range 1−60bar) attached to the upper housing. As a safety precaution, a safety release valve is fixed to the upper housing chamber and set at 65bar.

**Ignition**: Ignition of the flame is initiated by a short-duration hydrogen pilot flame and always performed at atmospheric pressure. High-pressure ignition could produce shock waves to propagate inside the chamber and could potentially warp the housing or cause damage to the windows. A thin Ni-Cr wire (1mm diameter) is connected to the end of a resistance coupled spark plug (Bosch) and current (12V and 10Amps) is passed until the wire radiates a bright glow. A short jet of hydrogen is injected across the glowing wire to ignite the pilot flame. In the event of an ignition failure, air should be used to purge the chamber and exhaust pipes of excess fuel. Failure to do so will cause ignition to occur in the exhaust pipes, from which pressure waves can propagate back into the burner and cause cracking of the windows or damage to the housing.

**Gas Flow**: The fresh gases for the flame and the co-flow of air flow into the burner from compressed gas cylinders. High-pressure mass flow meters (Bronkhorst model & E-7000 Digital Control Unit) with different flow rates are used for each individual gas. The
flow meter for the air co-flow has the largest capacity with a maximum flowrate of 100L/min (1bar@273K). Flow meters for the co-flow air and fuel (CH\textsubscript{4}) have a capacity of 10L/min and 1L/min, respectively. The diluted NO mixture and N\textsubscript{2} are controlled with flow meters with a maximum flowrate of 500mL/min. The NO mixture is used for seeding NO in the fresh gases and a 2% NO by volume diluted in N\textsubscript{2} buffer gas was used for the current study. The N\textsubscript{2} flowmeter is used to balance the overall flowrate of the fresh gases as the seeding amount of NO is varied in many of the experiments. The exact flowrates of the gases for a specific flame condition are critical parameters for stable burner operation. Optimized flowrates used in this study are documented in Appendix 2. The flowmeters are calibrated annually using manual bubble flowmeters (Kontess Glass Company). The air used in the fresh gases is checked for exact O\textsubscript{2} content in the lab using a diode laser oxygen analyzer (Oxygraph, O\textsubscript{2} analyzer) to ensure that accurate equivalence ratios are reflected in the experiment. A portion of all the tubing which connects the burner to the flowmeters is flexible to allow for vertical translation of the burner housing.

Changing Flame Settings: Changing equivalence ratios for the same pressure requires only adjusting the flowmeter settings. Full transition to a stable flame for the new settings requires about 2 minutes at 60bar, and less time at lower pressures. Shifting up in pressure requires more care. First, the flowrates (Appendix 2) are adjusted to the next pressure setting gradually while always maintaining a slightly rich equivalence ratio. The flame is visually monitored using a conventional CCD camera. Once the required flowrates for the higher pressure are reached, the needle valve is slowly closed to achieve the actual pressure inside the chamber. In the event of a blowoff or quenching of the flame at high-pressures, it is critical to evacuate the chamber fully and initiate a new ignition at atmospheric pressure with the main valve open. Shifting down in pressure requires a reverse procedure, but is more prone to flame instability and generally takes a longer time. For this reason, in most cases, downshifting of pressure was only used at the very end as a way to lower the pressure before extinguishing the flame when flame stability is not an issue. Acquiring a stable flame at a lower pressure is more quickly
achieved by completely extinguishing the flame and working back up from an atmospheric flame.

All the controls required for the operation of the burner are centralized to a single station away from direct view of the burner for safety considerations. Safety is a major concern and an issue of utmost priority in the operation of the high-pressure burner. The entire housing during operation is encased in transparent Pyrex bullet-proof shielding (~2cm in thickness) to protect the user in the unlikely event of a failure of a structural component during operation. Windows of the burner can also exhibit structural damage when the laser energy is tightly focused and the intensity exceeds the quartz threshold, and were routinely checked for damage by using laser scattering from a HeNe diode laser. Leakage of toxic chemicals (mainly NO for our experiments) is also a concern. A gas leak sensor (EIT 5300 for NO) is employed just above the chamber casing to monitor potential leaks.

3.1.2 Laser System

Light amplification by stimulated emission of radiation (LASER) is used as the primary source for perturbing specific energy states of target molecules in this study. Unique properties of laser light enable selective and quantitative probing of energy states by targeting specific transitions which are in resonance with the monochromatic frequency of the laser light. This light is generated by amplifying oscillating photons via stimulated emission. Therefore, the coherent output is comprised of photons that are identical in phase, direction and amplitude. The output beam is singularly directional, intense and monochromatic [100]. Short pulse lasers used in this study enable short excitation (<10ns) and detection times (<1μs) to minimize interference of continuous signals such as flame chemiluminescence and ambient room light. Furthermore, short-pulse lasers are capable of generating intense concentration of laser energy over a very short duration, enabling two dimensional measurements to be made over extended volumes.

Technology and understanding of lasers has greatly evolved over the last few decades and many different lasers are available commercially for practical use [101, 102].
**Experimental Facility and Procedure**

<table>
<thead>
<tr>
<th></th>
<th>Nd:YAG Laser</th>
<th>Dye Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacture and model</td>
<td><em>Quanta Ray GCR250</em></td>
<td><em>LAS LDL205</em></td>
</tr>
<tr>
<td>Laser medium</td>
<td>Nd(^{3+})-doped Yttrium-aluminum-garnet ((Y_3Al_5O_{12})) crystal</td>
<td>Fluorescent dye solution in organic solvent</td>
</tr>
<tr>
<td>Pumping source</td>
<td><em>Flash lamp</em></td>
<td><em>Nd:YAG</em></td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10Hz</td>
<td>10Hz</td>
</tr>
<tr>
<td>Laser transition</td>
<td>(Nd^{3+} \rightarrow ^4F_{3/2} \rightarrow ^4I_{11/2})</td>
<td>Dye (S_1 \rightarrow S_0)</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>1063nm, frequency tripled to 355nm</td>
<td>440–520nm, frequency doubled to 220–260nm</td>
</tr>
<tr>
<td>Laser bandwidth</td>
<td>(\Delta \nu \sim 6.6cm^{-1})</td>
<td>(\Delta \nu \sim .25cm^{-1})</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>500mJ/pulse @ 355nm</td>
<td>1–2mJ/pulse @ 226nm</td>
</tr>
<tr>
<td>Pulse length</td>
<td>7ns</td>
<td>7ns</td>
</tr>
</tbody>
</table>

**Table 3-1** Specifications of Nd:YAG and dye laser used in this study.

All lasers to date operate under the same principle of generating a population inversion between two energy states and then inducing fluorescence via stimulated emission of photons. Therefore, all lasers basically have three common features: Pump, Gain medium and Cavity. Gain medium is the essential material for generating a population inversion and subsequently emitting radiation. Depending on the medium, lasers are categorized as gas, liquid or solid-state lasers. The cavity is designed to maximize the amplification of light through the process of stimulated emission. Incoming photons induce emission of additional photons which are coherent and in the same direction. Typically, the cavity has two high-reflective mirrors on either end to enable multi-pass amplification. The pump source is used for supplying the energy required for population inversion. Depending on the laser system, the pump-source can be a light source, electric discharge, or an alternative means of energy exchange. The primary laser system used in this study is a two state dye laser pumped by a neodymium-doped yttrium-aluminum-garnet (Nd:YAG) laser. Specifications of the lasers used in this study are summarized in...
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table 3-1, followed by a brief discussion of the fundamentals concepts involved in the operation of the two lasers. A more detailed can be found in textbooks of Siegman [102] and Demtröder [15].

Nd:YAG Laser

The gain media for Nd:YAG lasers are Yttrium-aluminium-garnet (Y₃Al₅O₁₂) crystals, where approximately 1% of the Y³⁺ ions have been substituted by Nd³⁺ ions: otherwise known as triply ionized neodymium.

\[
\begin{align*}
4F_{3/2} & \quad 11502 \text{ cm}^{-1} \\
4I_{9/2} & \quad 2111 \text{ cm}^{-1}
\end{align*}
\]

Population inversion is created by pumping the population from a ground state (⁴I₉/₂) to excited upper states via flash lamps. Excited electrons quickly drop to the ⁴F₃/₂ level, which is also the upper level of the lasing transition. The molecules stay in the ⁴F₃/₂ level for a fairly long time (~230 msec) before relaxing to a lower level, during which time lasing can be initiated. The most probable lasing transition is to the ⁴I₁₁/₂ state, where a photon at 1064nm is emitted. Transition from ⁴I₁₁/₂ state to the ground state is fast, and therefore population inversion is easily established between the two lasing states. The overall dynamics can be best simplified using a four level model, and a schematic of the process is shown in Figure 3-5. For high power in pulsed operations, a Q-switch is

Figure 3-5 Four level model of an Nd:YAG laser.
Experimental Facility and Procedure

used. The Q-switch is comprised of a polarizer, a quarter-wave plate and a Pockels cell. It acts as an optical switch to maintain a high-loss condition in the cavity while the population inversion builds up. At the optimum point, a short current is applied to the Pockels cell. This changes the polarization characteristics of the resonating beam and the cavity is instantly switched to a low-loss condition to make full use of the inverted population. The temporal length of the current to the Pockels cell induces an ultra short (<10ns) and high intensity output.

In this study, 355nm from the Nd:YAG is used to pump the dye laser. The fundamental wavelength of the Nd:YAG is 1064nm. This is passed through an optically non-linear crystal, and depending on the polarization of the beam and the incident angle to the crystal axis (i.e., phase matching), doubling of the photon energy can occur. This process is called second harmonic generation (SHG). The doubled beam (532nm) can then be mixed with the fundamental beam (1064nm) to produce a third harmonic at 355nm as follows,

\[
\nu_{1064\text{nm}}^1 \rightarrow \nu_{532\text{nm}}^2
\]

\[
\nu_{1064\text{nm}}^1 + \nu_{532\text{nm}}^2 \rightarrow \nu_{355\text{nm}}^3.
\]

Dye Laser

Dye lasers are the most commonly used laser for providing tunable emission in the visible range. By using non-linear phase matching, visible output from a dye laser can be extended down to far UV wavelengths (<250nm). Dye lasers take advantage of organic dyes, which provide broad fluorescent linewidths (50–100nm). The dye is usually dissolved in an organic solvent and act as the laser medium while being circulated inside a transparent cell. The broad and continuous fluorescent features of organic dyes are caused by the large number of dense rotational and vibrational levels within each electronic state, which are subsequently collision-broadened by strong collision between the dye and the organic solvent. While the dye emission is broadband, dye lasers use a wavelength-dispersive optical element such as a diffraction grating or a prism in the laser cavity to selectively amplify light in a narrow bandwidth for tuning.
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The molecules in the dye are optically pumped to an excited state to establish a population inversion. This is typically done by using flashlamps or another laser. In this study, the dye laser is pumped using the output from an Nd:YAG laser. The characteristics of the laser pulse from a dye laser is directly related to that of the pump source, and short high energy pulses from the Nd:YAG are reflected in the final dye laser output. The excitation and de-excitation for a typical dye is a multi-level process, and a general schematic for the energy levels are shown in Figure 3-6. Optical pumping and laser emission takes place between the ground and first excited singlet electronic state $S_0$ and $S_1$. Population is rapidly shifted to $S_1$ state by internal conversion, and rapidly transition (vibrational relaxation) occurs out of $S_0$ to establish a population inversion. Intersystem crossing to adjacent triplet states ($T_1$) compete with the intended dynamics and reduces laser efficiency.

![Figure 3-6](image)

*Figure 3-6* Energy levels of typical organic laser dye. Inter System crossing (ISC) is shown to adjacent level $T_1$.

Primary transitions used in the study are $A-X(0,0), (0,1)$ and $(0,2)$ excitation of the NO molecule at 226nm, 235nm and 248nm, respectively. These three transitions are generated by using three different dyes: Coumarin 120 for 226nm, Coumarin 102 for 235nm and Coumarin 307 for 248nm. General specifications on these dyes and applied concentrations are listed in table 3-2. In addition, Figure 3-7 shows the tuning curves for the individual dyes, pumped with 355nm third harmonic of an Nd:YAG laser. The output of the dye laser is then doubled using a doubling unit to the desired wavelength in the
UV. The doubling unit consists of a nonlinear crystal ($\beta$-barium borate: $\beta$-BaB$_2$O$_4$ or BBO), compensator and a Pellin-Broka prism for isolation of the UV light.

### Table 3-2

<table>
<thead>
<tr>
<th>Chemical Comp.</th>
<th>Coumarin 120</th>
<th>Coumarin 102</th>
<th>Coumarin 307</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition in study</td>
<td>$NO A^2\Sigma^+ - X^2\Pi (0,0)$</td>
<td>$NO A^2\Sigma^+ - X^2\Pi (0,1)$</td>
<td>$NO A^2\Sigma^+ - X^2\Pi (0,2)$</td>
</tr>
<tr>
<td>Chemical Comp.</td>
<td>$C_{10}H_9NO_2$</td>
<td>$C_{16}H_{12}NO_2$</td>
<td>$C_{13}H_{12}NO_2F_3$</td>
</tr>
<tr>
<td>Solvent</td>
<td>Methanol</td>
<td>Methanol</td>
<td>Iso-Propanol</td>
</tr>
<tr>
<td>Max emission (nm)</td>
<td>440nm</td>
<td>481nm</td>
<td>500nm</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>14</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>Concentration used*</td>
<td>0.2g/L</td>
<td>0.4g/L</td>
<td>0.33g/L</td>
</tr>
</tbody>
</table>

Modern dye lasers usually use multi-stage amplification (typically two), employing two cells which sequentially amplify the final output. The first cell is coupled with a prism or a diffraction grating for simultaneous amplification and selective tuning of a specific wavelength. It is often referred to as the preamplifier. The following cells act purely to boost the narrowband beam through stimulated amplification. The dye laser used in this study was modified to use a Bethune cell [103] (3mm diameter) in the second amplification stage rather than an additional dye cell. Instead of a square optical encasement, a Bethune cell is cylindrical with the original beam traversing the length of the tube and the pump beam providing amplification from the sides. The Bethune cell eliminates the need to focus the pump beam on the dye cell and greatly reduces the effect of pointing instability in the pump laser in comparison to conventional dye lasers. Laser alignment and power optimization was carried out using a Molectron PM5100 power meter. The contribution of amplified spontaneous emission (ASE), a fraction of non coherent emission from the laser, was suppressed to less than 1% in our laser system by swiveling the preamplifier cell slightly to steer the ASE from the beampath. One drawback of a dye laser system is that organic dyes lose their strength over time and
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require changing. Dye lifetimes are especially short for Coumarin dyes pumped using high powered pulsed lasers (~50% decay in 2 hours). Cooling the dye circulators with heat-exchangers can help to minimize this decay.

![Emission curves for the laser dyes used in this study.](image)

**Figure 3-7** Emission curves for the laser dyes used in this study.

### 3.1.3 Detection System and Optical Setup

Two main experimental setups are used in this study: 1-D Line-imaging and 2-D PLIF-imaging. Schematics for both 1-D line-imaging and PLIF imaging configurations are shown in Figure 3-8 and Figure 3-9, respectively, for using excitation in the NO $A^2Σ−X^2Π(0,0)$ transition at 226nm.

For 1-D line-imaging measurement, the laser beam is weakly focused into a single point or narrow width light sheet using a combination of spherical or cylindrical lenses. Typically, the beam was focused along a line 3mm above the burner matrix just past the flame region. High-reflective wavelength-specific mirrors allow precise alignment of the beam into the flame.
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**Figure 3-8** Experimental setup for 1-D line imaging.

**Figure 3-9** Experimental setup for 2-D PLIF Imaging.
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The fluorescence signals are collected at right angles to the laser beam and focused using a $f=105\text{mm}$, $f/4.5$ achromatic UV-lens (Nikon, Nikkor-UV), dispersed spectrally through an imaging spectrometer (LaVision Chromex 250IS) and imaged onto the chip of an intensified CCD camera (LaVision Dynamight). A more detailed description of the detection system is included in this section. The spectrometer slit is aligned parallel to the laser beam and the final image obtained from the ICCD camera yields 1-D spatial resolution along one axis and emission wavelength on the other axis. Spectral dispersion of the emission spectra enables a visual evaluation of the excitation line used. For this reason, 1-D line-imaging is utilized as a key data acquisition protocol in all the subsequent chapters of this thesis.

For 2-D PLIF imaging measurements, the laser is optically stretched into a vertical sheet (i.e., $0.5\text{mm}\times 15\text{mm}$) and imaged directly using an ICCD camera with different filter sets for suppression of Rayleigh scattering and bandpass filtering. As can be seen in both Figure 3-8 and Figure 3-9, the intensity of the laser beam is monitored with a fast photodiode (LaVision CIO16 energy monitor).

**Intensified CCD Camera**

The combination of a CCD detector and image intensifier provides enhanced sensitivity to the point of measuring single photons down to far UV ($<200\text{nm}$). Most importantly, an ICCD camera is capable of extremely fast shutter speeds of several ns (i.e., optical gating). The image intensifier is composed of three parts: photo cathode, micro channel plate (MCP) and phosphor. The photons initially strike the photo cathode, and electrons are generated and accelerated towards the MCP within a short intensifier gate period. The MCP is charged with a high voltage and amplifies the number of electrons via electron cascade. The gain is controlled by the voltage of the MCP. After leaving the MCP, the electron cloud is attracted by a high voltage ($\sim 6000\text{V}$) onto the phosphor. The phosphor converts the electrons into ‘green’ photons, which are subsequently imaged onto the CCD chip. Two intensified cameras (LaVision Flamestar III and Dynamight) were used for this study and general specifications are listed in table 3.
### Experimental Facility and Procedure

<table>
<thead>
<tr>
<th></th>
<th>LaVision Flamestar III</th>
<th>LaVision Dynamight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum gating (ns)</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Resolution (pixels)</td>
<td>1024 × 1024 pixels</td>
<td>1024 × 1024 pixels</td>
</tr>
<tr>
<td>Spectral response (nm)</td>
<td>180–900</td>
<td>180–800</td>
</tr>
<tr>
<td>Pixel size (μm)</td>
<td>24 × 24</td>
<td>13 × 13</td>
</tr>
<tr>
<td>Sensitivity (max)</td>
<td>600 counts/photo electron</td>
<td>2000 counts/photo electron</td>
</tr>
<tr>
<td>Cooling</td>
<td>Peltier</td>
<td>Peltier &amp; water circulation</td>
</tr>
</tbody>
</table>

**Table 3-3** Specifications of intensified cameras used in this study.

### Imaging Spectrometer

LIF emission can be dispersed on a diffraction grating of a spectrometer to reveal the contribution of different spectral components. Spectrometers can have many different configurations. The Chromex 250IS (LaVision) spectrometer used in this study utilizes a Czerny-Turner design where the light is focused through a variable entrance slit, collimated by a focusing mirror, dispersed on the grating. Three gratings (68×68mm) are positioned around a turning mount, and can be alternatively rotated to provide varying levels of dispersed spectral resolution and range. The three gratings are 300gr/mm (blazed at 250), 600gr/mm (blazed at 300nm) and 2400gr/mm holographic (blazed at 250nm). The dispersed light from the grating is re-collimated and imaged onto the CCD chip of the camera. Though not used in this study, the spectrometer also is able to scan across the emission spectrum by rotating the grating mount between each data acquisition. Wavelength steps of 0.3nm steps can be achieved using the 600gr/mm grating.

### 3.2 Data Acquisition and Processing

The system used for data acquisition and processing is discussed in this section. The experimental setup for data acquisition involves synchronization of laser pulses with the camera exposure and intensifier, readout of the camera system, simultaneous...
monitoring of the laser energy, control of the spectrometer settings, and implementation of proprietary acquisition routines. For data processing, a macro language driven shell (DaVis, LaVision) is used as the primary interface and processing tool. Additional computational routines and data files are accessed via DaVis and utilized for data processing, including spectral simulations for the relevant chemical species. An overview of the data acquisition and processing involved in this study are shown in Figure 3-10.

**Figure 3-10** Data acquisition and processing overview.

**Data Acquisition**
DaVis is a CCD image acquisition and processing program developed by LaVision. It is specifically designed for use with LaVision cameras including the Flamestar III and Dynamight used in this study, and can accommodate the integration and operation of other hardware (spectrometer, lasers, stepmotors etc.). In our case, the control of both the camera and spectrometer settings is carried out by this system. For data acquisition, DaVis provides control of timing schemes for the camera operation and synchronization.
of laser systems via a TTL I/O card. The triggering scheme of the current study is initiated by a pulse from the Nd:YAG laser, which is used to trigger both the camera and intensifier within a given gate width (50ns) and after a time delay. The CCD chip is read out and data are transferred to be processed via the I/O card. Simultaneously, laser energy from photodiodes are also read into DaVis and stored as transient profiles for laser analysis. Finally, output triggers relayed to the dye laser can change the laser wavelength (if required for a scan) and initiate the acquisition of the next image. Proprietary macros were used to control the overall data acquisition process to monitor the incoming data realtime, and for performing basic data processing steps for integrity evaluation.

**Data Processing**

DaVis offers many default subroutines for processing spectroscopic data, and for image processing. More complex processing functions can be applied by using a macro programming language, ‘Command Language (CL)’, from the DaVis shell. The CL-macro provides an efficient way to program specific subroutines into the analysis, as well a flexible means to control the input and output of data and interfacing with external software for data processing. All the data and image processing included in this thesis were applied using CL-macro programming and executed from the DaVis user interface. Additional programs (i.e., LIFSim (ver 3.16), Matlab etc.) are also linked to the main interface via CL-macros for specific data analysis steps. These include computational simulation of NO and O$_2$ (all chapters), computational fitting of emission spectra using a non-linear least square fitting routine (chapters 4, 5 and 6), computation fitting of excitation spectra (chapter 6), sensitivity analysis of multi-line fitting thermometry (chapter 6) and multi-window transmission analysis using simulated filters (chapter 7).
Chapter 3
Chapter 4 Optimization of Excitation Strategies

In this chapter, a comprehensive study of excitation strategies for laser-induced fluorescence detection of nitric oxide (NO) is presented. Selected transitions in the $A-X(0,0)$, (0,1) and (0,2) bands of NO are compared in terms of signal strength, transmission qualities, interference from $O_2$ and $CO_2$ LIF, and pressure and temperature dependence. While high-pressure conditions present formidable challenges for quantitative LIF, careful optimization of the excitation strategy can minimize many of the complications. The discussion presented in this chapter is based on spectroscopic measurements in laminar premixed methane-air flames at pressures between 1 and 60 bar and on spectral simulations of NO and $O_2$ LIF. The work presented in this section has been conducted in collaboration with researchers at the University of Heidelberg, and discussion is based on results published in the following references: [104-107].

4.1 Background

An overview of the problems which arise when applying LIF diagnostics to high-pressure flames, and an investigation of selective excitation strategies are presented here. Laser-induced fluorescence (LIF) is an important tool to help understand nitric oxide (NO) formation in both practical combustion systems and laboratory flames [1, 2, 12]. Investigations aim to develop engineering solutions to minimize NO effluent, optimize combustor efficiency, as well as to develop and validate chemical kinetics models of NO formation and destruction. Practical combustors (internal combustion engines, gas turbines, etc.) generally operate under high-temperature and high-pressure conditions, which can significantly impact the interpretation of LIF signals. Therefore, quantitative LIF diagnostics requires correction for the influence of temperature, pressure, and the concentration of all other species. In particular, complexities caused by high-pressure
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offer a significant challenge in applying LIF. To minimize potential errors resulting from high-pressure effects, selective excitation using an optimized transition line of NO is required.

4.1.1 NO $A$–$X$ Excitation

Different approaches for NO excitation suggested in the literature mainly use transitions in the $D$–$X$(0,1) band and several in the $A$–$X$ vibrational bands of NO. There is, however, a lack of guidelines as to the performance of individual transitions in a given diagnostic condition. The aim of this chapter is to compare NO $A$–$X$(0,0), (0,1) and (0,2) strategies and individual transitions within each strategy to provide optimized excitation and detection strategies for NO-LIF in high-pressure combustion. By providing an evaluation of excitation strategies for well defined conditions, performance levels when applied to practical combustors can be predicted. Transitions in the NO $D$–$X$(0,1) band are ruled out due to their transmission inefficiencies in high-pressure flames.

![Potential energy diagram of the NO $X$, $A$ and $D$ states. Arrows indicate different excitation strategies used in this study. 1. $A$–$X$(0,0) at 226nm 2. $A$–$X$(0,1) at 235nm 3. $A$–$X$(0,2) at 248nm.](image-url)
Figure 4-1 shows a potential energy diagram of the relevant electronic states of NO with transitions typically used for LIF diagnostics. Population density in the ground $X^2Π$ electronic state is mostly distributed in the $v''=0$ level at ambient temperatures. At typical combustion temperatures (~2000K), sufficient redistribution can populate higher vibrational levels. Considering the feasibility of fluorescence signal strength, vibrational levels up to $v''=2$ level in the lower electronic state can be used for excitation in NO LIF diagnostics. Strategies for NO $A−X(0,0)$, (0,1) and (0,2) excitation schemes are shown in Figure 4-1 as 1,2 and 3, respectively.

![Figure 4-2](image.png)

**Figure 4-2** Excitation spectra for NO $A−X(0,0)$, (0,1) and (0,2) vibrational bands.

Once the molecule is excited to the $v'=0$ level in the upper electronic state, fluorescence emission from the $A^2Σ^+$ state can occur into multiple vibrational bands in the lower $X^2Π$ state, providing flexibility in the choice of detection wavelength regions. For $A−X(0,1)$ and (0,2) transitions, the fluorescence process out of the $A$ state can occur to vibrational levels ($v''$) in the $X$ state as determined via the Frank Condon overlap of the two electronic states. Resulting emission in this case produces photons with more energy than the initial excitation photons of the laser, allowing the detection wavelength region to be “blue-shifted” (detection at lower wavelength than laser beam) relative to
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the excitation wavelength. NO LIF strategies using both “blue-shifted” and “red-shifted” detection schemes are discussed in the following sections.

<table>
<thead>
<tr>
<th>$A-X$ band</th>
<th>Features</th>
<th>Short name</th>
<th>Ground State Energy $\epsilon/k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0) 224.82nm</td>
<td>$R_1+Q_{21}(26.5)$, $Q_2+R_{12}(34.5)$, $P_1(40.5)$</td>
<td>High-T</td>
<td>1750–4032K</td>
</tr>
<tr>
<td>(0,0) 225.25nm</td>
<td>$R_1+Q_{21}(21.5)$</td>
<td>Sick [61]</td>
<td>1161K</td>
</tr>
<tr>
<td>(0,0) 225.58nm</td>
<td>$Q_2(26.5)$</td>
<td>Laurendeau [9]</td>
<td>1967K</td>
</tr>
<tr>
<td>(0,0) 226.03nm</td>
<td>$P_1(23.5)$, $Q_1+P_{21}(14.5)$, $Q_2+R_{12}(20.5)$</td>
<td>DiRosa [8]</td>
<td>540–1381K</td>
</tr>
<tr>
<td>(0,0) 226.87nm</td>
<td>$P_2+Q_{12}(1.5–4.5)$</td>
<td>Low-T</td>
<td>178–232K</td>
</tr>
<tr>
<td>(0,1) 235.55nm</td>
<td>$R_1+Q_{21}(16.5)$, $P_2+Q_{12}(32.5)$, $P_{21}(22.5)$, $O_{12}(40.5)$</td>
<td>A</td>
<td>3384–6950K</td>
</tr>
<tr>
<td>(0,1) 235.87nm</td>
<td>$P_1(25.5)$, $R_1+Q_{21}(11.5)$, $Q_1+P_{21}(17.5)$</td>
<td>B</td>
<td>3040–4305K</td>
</tr>
<tr>
<td>(0,1) 236.22nm</td>
<td>$R_1+Q_{21}(22.5)$, $Q_1+P_{21}(8.5)$, $Q_2+R_{12}(17.5)$</td>
<td>Jamette [66]</td>
<td>2718–3660K</td>
</tr>
<tr>
<td>(0,2) 247.94nm</td>
<td>$O_{12}(8.5–10.5)$ bandhead</td>
<td>Schulz [108]</td>
<td>5680–5820K</td>
</tr>
</tbody>
</table>

Table 4-1 The nine candidate transitions used in this work.

There are hundreds of rotational transitions which can be used for LIF diagnostics in the $A-X(0,0)$, (0,1) and (0,2) bands of NO using narrowband high-powered lasers. Figure 4-2 shows a simulated (LIFSim [10]) excitation spectrum of NO in the relevant wavelength region where the semi-resolved rotational features are visible in each vibrational band. Among these choices, nine promising transitions are singled out as providing optimal performance in high-pressure combustion. These transitions have shown promising characteristics mainly for signal strength and minimized interference from O$_2$ signals. Five transitions are found within the $A-X(0,0)$ band, three in the $A-X(0,1)$ band and one additional transition is located in the $A-X(0,2)$ band. Five of those transitions have been previously investigated in the literature for high-pressure
Optimization of Excitation Strategies

NO-diagnostics. Four other new transitions were identified using experimental data and spectral simulations from this study. All nine transitions are summarized in Table 4-1. The short names given to the individual transitions are used in this chapter for convenience. Detailed discussions of these transitions and comparisons are provided in the following sections, providing a clear guideline for optimization of excitation strategies in practical combustion conditions.

4.1.2 Problems Caused by High Pressure

Applying NO-LIF in high-pressure flames is confronted by a number of difficulties compared to that of atmospheric-pressure flames. Understanding the problems involved and quantifying the extent of these undesirable effects can provide a valuable guideline for selection of the excitation strategy.

![Absorption cross-sections of CO₂ and H₂O as a function of temperature and wavelength. Ref. [109].](image)

**Figure 4-3** Absorption cross-sections of CO₂ and H₂O as a function of temperature and wavelength. Ref. [109].

**Transmission Problems**

In many high-pressure combustion systems, laser and signal attenuation have been reported to be major problems. Electronic excitation of NO from sufficiently populated states requires short UV wavelengths around 193 nm in the $D−X(0,1)$ band or at 226, 237, 248 nm for excitation in the $A−X(0,0)$, (0,1) and (0,2) bands, respectively. Recent
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experiments showed that hot CO$_2$ and H$_2$O exhibit strong absorption characteristics in this spectral range [109, 110]. These triatomic compounds exhibit broadband absorption behavior with cross sections increasing with temperature and decreasing with wavelength. Figure 4-3 demonstrates this phenomenon, where absorption cross sections for both CO$_2$ and H$_2$O have been plotted as a function of temperature and wavelength. For the wavelength range and flame temperatures relevant to the current study, CO$_2$ is the more dominant absorber and accounts for most (>90%) of the attenuation effects at pressure above 20bar. Transmission problems caused by the abundance of CO$_2$ and H$_2$O in most post combustion gases limit the choice of NO excitation-detection strategy and often rule out the application of $D-X$ excitation at high pressures due to severe absorption at 193nm. A more feasible solution is found in the NO $A-X$ system using different rotational transitions in the (0,0) band as well as transitions in the (0,1) and (0,2) bands (with various detection strategies), which further reduce laser attenuation. In practice, the attenuation caused by this absorption results in asymmetric images and distorted fluoresce signals, which require correction by using absorption coefficients of both CO$_2$ and H$_2$O.

$O_2$-LIF Interference

A key concern when choosing a potential wavelength for NO excitation is the suppression of spectral overlap with excitation of other species that might result in interfering LIF signal. Hot O$_2$ is an important contributor to LIF interference in lean and non-premixed flames. The $B^3\Sigma^- - X^3\Sigma^+$ Schumann-Runge bands of O$_2$ are pervasive in the relevant excitation wavelength region and overlap with the $A^2\Sigma^+ - X^2\Pi$ NO gamma bands [17] over a wide range of excitation wavelengths. Measurements with spectrally resolved detection of the fluorescence provide a way of distinguishing between different signal contributions based on their spectral signature. However, this approach is generally limited to single-point or line-resolved 1-D line-imaging measurements. For PLIF imaging measurements bandpass filters minimize the contribution of O$_2$ interference, but are typically not suited to fully separate the overlapping signal intensities.

The ratio of O$_2$-LIF background increases with pressure for two reasons: variation in fluorescence quantum yield and variation in spectral overlap with the laser
Optimization of Excitation Strategies

profile due to line-broadening. The effective fluorescence lifetime of NO decreases linearly with pressure due to collisional quenching [95], while the effective fluorescence lifetime of excited $O_2$ is limited by its fast predissociation [92] and is thus mostly pressure-independent up to a pressure of ~25 bar [91]. Hence, the relative fluorescence quantum yield and therefore the ratio of the $O_2$ and NO LIF signals increase with pressure. In addition, pressure broadening of excitation lines increases the spectral overlap between NO and $O_2$ excitation, making the choice of excitation wavelengths more critical at high pressure.

**CO$_2$-LIF Interference**

CO$_2$ broadband emission was recently identified in lean, stoichoimetric, and rich high-pressure methane-air and methane-oxygen-argon flames and is described in detail in the next chapter of the thesis. This signal consists of a broad (200–450 nm) continuum with a faint superimposed band structure, and its fluorescence yield is constant for pressures up to at least 40 bar. As with $O_2$, the relative influence of the CO$_2$ LIF increases with pressure as the NO fluorescence yield is mainly driven by quenching effects and proportional to $1/p$. Although the CO$_2$ signal is comparatively weak, it can become an important contribution to the overall signal when detection over wide spectral ranges is used. CO$_2$ interference is particularly pronounced for transitions with weaker NO signal strengths as will be shown in the following sections.

**Hydrocarbon Emission in Rich Flames**

In rich and non-premixed flames additional broad-band fluorescence interference has been observed which is usually attributed to polycyclic aromatic hydrocarbons (PAHs) and partially burned hydrocarbons (aldehydes, ketones) [111]. In sooting flames at high laser energies, interference by LIF of laser-generated C$_2$ has also been reported [112]. Laser-induced incandescence (LII) is observed in sooting flames [113], however at considerably higher wavelengths (>350 nm) than normally used for NO detection (<300 nm). The work reported here concentrates on premixed flames with $\phi<1.2$ where the PAH interference is relatively small. Research on CO$_2$ LIF [114] shows the onset of strong PAH interference near $\phi=1.6$. 

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Pressure Broadening and Shifting

As the pressure increases, the excitation spectra are significantly altered by collisional broadening and shifting. An example of this effect is shown in Figure 4-4, where simulations of excitation spectra (225.975–226.08nm) is shown for pressures ranging from 1–60bar.

![Figure 4-4](image)

**Figure 4-4** NO-LIF excitation spectra for an excitation wavelength range of 225.975–226.08nm in the $A-X(0,0)$ band with pressure variation of 1–60bar. Strong influence of pressure broadening and shifting can be seen.

It can be seen that neighboring rotational lines overlap with one another with a general decrease in intensity. The line-broadening additionally results in reduced spectral overlap of laser-lines with the absorption features, which reduces the signal strengths. While exciting single rotational transitions can be achieved at atmospheric pressure, multiple transition lines are excited simultaneously at high-pressures due to the blending of neighboring rotational lines. The line-broadening additionally results in reduced spectral overlap of laser-lines with the absorption features, which reduces the signal strengths. In addition to the decrease of signal, temperature dependence of different transitions also changes from added contribution of nearby lines and the pressure shift of the excitation spectra. LIF simulation models must be able to accurately model this effect. NO is more
affected by line-broadening than O₂, again due to the fast predissociation of O₂ where the fluorescence yield is less driven by quenching and rely less on pressure.

4.2 Experiment

The experiments were conducted in the High Temperature Gasdynamics Laboratory at Stanford University using the high-pressure burner previously described in Section 3.1. A 1-D line-imaging setup was used and investigations were performed for fuel/air equivalence ratios of $\phi=0.83$, 0.93, 1.03 and 1.13. All measurements were carried out with 300ppm NO seeded to the feedstock gases to mimic the conditions of a practical combustor more accurately. Optical access via the fused silica windows was used for probing of the combustion gases using laser light and for detection of the fluorescence signal. A Nd:YAG-pumped (Quanta Ray GCR250) frequency-doubled (BBO) dye laser (LAS, LDL205) produced laser light (ca. 1mJ, 0.25cm⁻¹ full width at half maximum, FWHM) at 224–227nm for NO $A-X(0,0)$ excitation (Coumarin 120 dye) [105], 233–238nm for $A-X(0,1)$ excitation (Coumarin 102 dye) [106], and 245–248nm for $A-X(0,2)$ excitation (Coumarin 307 dye). The beam was weakly focused (0.5x0.5mm²) along a line and aligned parallel to the burner surface, passing through the center of the flame 2mm above the burner matrix. The pulse energy was measured with a photodiode (LaVision). A schematic of the 1-D line-imaging setup was previously shown in Figure 3-8.

Fluorescence signals were collected at right angles to the laser beam and line-imaged with a $f=105$mm, $f/4.5$ achromatic UV lens (Nikon, Nikkor-UV) onto the horizontal entrance slit of a 250mm imaging spectrometer (Chromex 250IS) equipped with a 600grooves/mm grating. The dispersed fluorescence signals were detected with an intensified CCD camera (LaVision, FlameStar III). The transitions investigated in each band are summarized in Table 4-1. The laser was tuned to record excitation spectra around these specific NO transitions within the $A-X$ bands. The spectral range was varied from 0.03nm to 0.06nm between 1 and 60bar to account for pressure broadening. Similarly, spectral resolution was also increased as a function of pressure as the broadened spectra becomes less defined and requires fewer data points for reconstruction.
The signal was averaged over 20–50 laser pulses for each excitation wavelength and stored for further evaluation before scanning the laser to the next wavelength. The spectra were corrected for variations in laser pulse energy.

4.3 Data and Evaluation

4.3.1 Spectrally Resolved 1-D Imaging

Spectrally resolved 1-D line-imaging data acquisition and processing are discussed here. Examination of individual transitions among the hundreds of candidates in the $A-X$ system requires an extensive experimental effort, and while specific experimental details regarding each strategy vary slightly, the main concept involves obtaining spectrally resolved images and reconstructing excitation and emission charts. The laser beam aligned parallel to the slit of the imaging spectrometer and focused with the achromatic lens, and the dispersed light is imaged onto an ICCD camera. The camera initially detects images with the spatial resolution along the horizontal path of the laser beam through the flame on one axis and spectral resolution showing emission spectra on the second axis. Two of these images are shown in Figure 4-5 (a) for typical situations in a lean 60 bar flame with “DiRosa” and “Sick” excitation in the $A-X$ band, respectively.

The central area of the flame, where temperature and concentrations are homogeneous is then chosen (marked by the lines in Figure 4-5) and integrated over the spatial axis producing the resolved fluorescence spectrum shown in the figure. Each of these spectra becomes a single line in the two dimensional excitation-fluorescence chart shown below in Figure 4-5 (b). After scanning the excitation laser to the next wavelength, the next “line” is recorded and added to the 2-D chart. The resulting two-dimensional excitation-emission charts show excitation and fluorescence wavelengths on the opposite axis with the intensity values shown as a gray scale. This representation contains the full spectral information, and allows later evaluation of excitation as well as emission spectra with arbitrarily selected bandpass. Note the interference from $O_2$ LIF at the “Sick” excitation is evident in the resolved fluorescence shown in Figure 4-5 (a). Profiles along the excitation frequency coordinate yields excitation spectra, where the 'bandpass' of the
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detection can be arbitrarily selected over the entire fluorescence range. Similarly, fluorescence spectra can be extracted with the excitation frequency being fixed at a given value. Figure 4-5 (b) gives an example for a 2-D spectrum near the “Sick” transition for $p=40\text{bar}$ and $\phi=0.83$.

![Figure 4-5](image)

**Figure 4-5** Construction of an excitation-emission chart in a 60bar, $\phi=0.83$ CH$_4$/air flame. Top panel (a) shows readout from CCD with spectrally resolved emission on the x-axis and spatial information on the y-axis for “DiRosa” and “Sick” excitation lines. The region between the white lines in (a) are averaged for construction of individual lines in the excitation emission chart (b).

Note the difference in the scale of excitation and emission wavelength axis. The strong emission signal at 226nm is due to elastically scattered laser light. Emission from the NO $A-X(0,0)$ band also contributes to this signal. The vibrational progression of the NO fluorescence in the $A-X$ band can clearly be seen, and is easily be distinguished from the vibrational progression of the interference O$_2$ $B-X$ fluorescence.
Once the key transitions are identified, short excitation scans in the wavelength region of the candidate lines are performed. An example of excitation-emission charts for the three transitions in the $A-X(0,1)$ band is shown in Figure 4-6 for all investigated pressures from 1–60bar and equivalence ratios from 0.83–1.13. For all the conditions, the feedstock gases are seeded with 300ppm of NO. The charts show major trends in signal strength and interference. On the emission ($x$) axis, we find strong signal from Rayleigh scattering around 235nm. The vibrational progressions of the NO $A-X$ and the $O_2 B-X$ emissions can clearly be seen and distinguished, they occur both blue-shifted and red-shifted from the excitation wavelength. NO emission gets weaker with increasing pressure (due to the variation in excitation efficiency, whereas the effects of fluorescence quantum yield and NO number density cancel) and, at high pressures, weaker with increasing equivalence ratio (due to a decrease in NO concentration caused by reburn reactions that are known to be more efficient in rich flames [115]). $O_2$ emission gets stronger with increasing pressure (which is an effect of fluorescence

### Figure 4-6

Excitation-emission charts for excitation wavelengths around the three $A-X(0,1)$ candidate transitions for all investigated pressures and equivalence ratios.
quantum yield and number density; $O_2$ is excited to predissociative states) and weaker with increasing equivalence ratio (due to a decrease in $O_2$ equilibrium concentration in the burnt gases).

### 4.3.2 Excitation Spectra

Excitation spectra can be extracted by employing a detection bandpass around the maximum emission band of NO LIF and taking a profile in the excitation (y) axis of the excitation-emission chart. Fluorescence excitation spectra for the transitions investigated in the $A-X(0,0)$ and $(0,1)$ bands are shown in Figure 4-7. The detection bandpass is chosen to minimize the contribution of $O_2$ LIF in the emission to minimize interference. Collisional line-broadening and shifting, which has been investigated in detail for the NO molecule [20-22], can be clearly seen in Figure 4-7. At the same time, line-broadening becomes significant, leading to a loss in rotational structure for pressures $\geq 10$ bar which is especially evident for the double peak of the Jamette transition feature in the $A-X(0,1)$ band. It is interesting to note that the peak signal strength increases slightly between 1 and 5 bar and then decreases again for increasing pressure as discussed in the previous section.

An optimized strategy for NO detection should involve excitation at a wavelength yielding maximum signal strength for each individual pressure. From Figure 4-7 it is evident that this can only be achieved by tuning the laser by several wavenumbers as the pressure increases from 1 to 60 bar. In practical applications, however, pressure often varies rapidly (e.g., internal combustion engines). Here a fixed excitation wavelength must be chosen. The resulting signal loss is most pronounced for pressures between 1 and 5 bar due to the simultaneous action of pressure broadening and -shift. Interestingly, this effect is strongly reduced when using the “Jamette” transition due to its double peak. The other candidates, on the other hand, show constant or even decreasing signal strength between 1 and 10 bar if the laser wavelength is held fixed at the 1 bar peak position. The variation of signal strength with pressure can be described using collisional broadening and shifting models [10]. Therefore, the effect can be corrected for in practical applications with known or separately measured pressure even if total signal is reduced due to non-optimized excitation.
4.3.3 Emission Spectra and Assessment of Interference Signals

Fluorescence emission spectra are extracted as horizontal profiles from the two-dimensional excitation-emission charts. Depending on where the profile is extracted, arbitrary excitation wavelengths can be selected. Spectrally resolved emission spectra enable visual confirmation of both NO-LIF intensity and relative contribution from alternative species and from laser scattering. Therefore, emission spectra are exclusively used for evaluating the performance of various excitation strategies. Typical emission spectra for transitions in the \( A-X(0,0) \), (0,1) and (0,2) strategies are shown in Figure 4-8.
Figure 4-8 Examples of the nonlinear least-square fit of simulated NO, O₂, CO₂, and Rayleigh (Ray.) emission spectra (represented as Voigt lineshapes) for the investigated excitation strategies at $p=60$bar, $\phi=0.83$.

The emission spectra were obtained by using excitation wavelengths corresponding to maximum NO-LIF intensities to separate and quantify the overlapping LIF signals of NO, O₂, and CO₂. The separate contributions from these sources are shown in Figure 4-8. Raman signals were not observed in the hot flame gases (the laser was polarized
horizontally for maximum suppression of the Raman signal). The experimental data were corrected for the wavelength-dependent detection efficiency and signal absorption from hot exhaust gases [109]. A non-linear least-square fitting procedure was used to separate the various overlapping LIF spectra and the contribution of elastically scattered light (Rayleigh), and to account for the (Voigt-type) spectrograph slit function. The intensities of simulated NO- and O₂-LIF emission spectra, experimental CO₂-LIF emission spectra [10], and a Rayleigh signal were simultaneously fit to the experimental data. The O₂-LIF emission spectra are complex due to overlapping absorption lines leading to simultaneous excitation into multiple vibrational states. Furthermore, vibrational energy transfer in the upper electronic B state was evident from the O₂-LIF emission structure. Therefore, emission signals from multiple upper vibrational O₂ B-states were fit independently. The ability to separate the spectra in different components (CO₂, O₂ and Rayleigh) enables quantitative assessment of interference levels for specific detection bandpass and direct comparison of excitation strategies can be made. Emission spectra itself can be used as a detection strategy and can be used for providing spectrally resolved information along a line by aligning the spectrometer slit parallel to the traversing path of the laser beam. More detailed discussion regarding using 1-D line-imaging for diagnostics will be addressed in Chapter 7.

4.3.4 Quantification of NO-LIF Signals

Despite constant NO seeding (300ppm in the fresh gases), the actual NO concentrations decrease in rich flames due to NO-reburn chemistry. The actual NO concentration past the flame front cannot be assumed as a sum of the natural NO formed and the seeded NO. More precisely, the NO experiences a slight reburn just before the flame front and then immediate recovery through a reverse reaction, usually leading to levels which are higher than the seeded amount and less than what would be additionally predicted due to the nascent formation of NO. Furthermore, NO-LIF signal yield depends on temperature, pressure, and equivalence ratio. Thus the ratio of NO-LIF signal to background signal is biased for different flame conditions. To enable an accurate comparison, the NO-LIF signal strength measured in the φ=0.93 flames is quantified using the temperature and concentration data using multi-line NO-LIF fitting [116] and
assuming an equivalence ratio dependent reburn factor of 10% of the seeded NO in these slightly lean flames. This assumption is in good agreement with Chemkin calculations using Premix and GRI-Mech 3.0. From the derived NO concentration value at $\phi=0.93$, the LIF signal of 300ppm NO is calculated for all equivalence ratios. The variation of quenching rate is considered using calculations of equilibrium exhaust gas compositions. These evaluations are performed individually for each investigated pressure. By quantifying exact LIF signal for 300ppm concentration of NO, we can compare the O$_2$ and CO$_2$ background signal strengths to the LIF signal of 300ppm NO for our flame conditions.

4.4 Study of NO $A-X(0,0),(0,1)$ and (0,2) Excitation Strategies

Detailed study of individual transition lines in the $A-X(0,0)$, (0,1) and (0,2) strategies is presented in this section. Transitions in each of the vibrational bands are compared by using emission spectrum fitting (Figure 4-8) and NO quantification as described above. Different transitions are compared in terms of signal strength, transmission qualities, interference from O$_2$ and CO$_2$, and temperature and pressure dependence. In Section 4.5, a comparison of the most promising transitions from each vibrational band is presented.

4.4.1 $A-X(0,0)$ Excitation

There are five transitions which have been singled out as “promising” from the $A-X(0,0)$ band and investigated in this section. They are listed in table 4-1 and have been given short names, “DiRosa”, “Sick”, “Laurendeau”, “High T” and “Low T”. Among the five, the DiRosa, Sick and Laurendeau lines have been previously applied in high-pressure NO-LIF measurements in the literature (referenced in table 4-1), while the High T and Low T lines have been newly identified and named accordingly for their sensitivities to different temperature ranges.

*NO Signal Strength using $A-X(0,0)$ excitation*
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To evaluate the relative NO signal strength for the different transitions, a detection bandpass range from 230 to 253nm was chosen, which includes the NO $A-X(0,1)$ and $(0,2)$ bands as well as three $O_2 B-X$ bands. This represents the most important bandpass for NO detection for practical applications (imaging as well as point-wise detection) because of the large Franck Condon factors of the NO $(0,1)$ and $(0,2)$ bands [117], which provide strong signals and maximum NO/O$_2$ LIF ratios. The total NO signal strengths in the bandpass region from 230–253 nm for the investigated flames are shown in Figure 4-9.

Figure 4-9 Total NO-LIF signal strength in the 232–252nm bandpass region for the five $A-X(0,0)$ candidates in $p=1–60$bar, $\phi=0.83–1.13$ flames.

For a given flame condition (in terms of pressure, equivalence ratio) the absolute NO and O$_2$ number densities as well as the temperature are identical for all candidates enabling a direct relative comparison. Figure 4-9 reveals a large difference in signal strengths for the different candidates. Generally, transitions that consist of multiple overlapping lines (like the “DiRosa”, “High-T” and “Low-T” features) give higher signal intensities at low
Optimization of Excitation Strategies

pressures (≤10bar) before pressure broadening becomes dominant. In general, the Dirosa line exhibited the best qualities in terms of providing high signal intensities.

**NO Signal Interference using $A-X(0,0)$ excitation**

As previously mentioned, the main interference to the NO LIF signal comes from LIF of O$_2$ and CO$_2$ for the flame conditions used in this study. By using spectrally resolved emission spectra and a specific detection bandpass (230–253nm), we can quantify the contribution of both species. Quantitative contribution of interference to the LIF signal of 300ppm NO for the different strategies for lean ($\phi=0.83$) and rich ($\phi=1.13$) flames as a function of pressure (1–60bar) are shown in Figure 4-10. Three quantities plotted are overall signal purities for NO (NO/(total)), O$_2$ (O$_2$/(total)) and CO$_2$ (CO$_2$/(total)) where total signal=NO+O$_2$+CO$_2$. The signal purity of NO is of particular concern and is plotted for the five transitions in Figure 4-11 for a more direct comparison between different transitions. It can be seen that the interference strongly increases with pressure. For nitric oxide, the decrease in the fluorescence yield caused by collisional quenching is cancelled by the increase in number density as the pressure is increased. However, pressure broadening effects reduce the overall intensity of the signal. For O$_2$ and CO$_2$, the LIF intensity is more linearly dependent on pressure since the fluorescence quantum yield stays approximately constant.

The contribution from CO$_2$ LIF is relatively small due to the strong NO signal strengths with $A-X(0,0)$ excitation (CO$_2$ interference is more relevant to $A-X(0,1)$ and $A-X(0,2)$ transitions). Therefore, the five candidate transitions had been chosen mainly to effectively suppress O$_2$ interference. Still, from Figure 4-10 a surprisingly large difference between the candidates becomes evident. While excitation of the “Laurenseau” and “Sick” transitions leads to strong oxygen interference (up to 29% for the highest pressure and lowest equivalence ratio investigated), excitation of the “DiRosa” transition under the same conditions reduces the interference to ≤8%. With an interference of only 16% for the worst case condition, the "High-T" transition has a clear advantage over the “Sick” transition. With ≤15% O$_2$-LIF interference, the “Low-T” transition provides an intermediate performance.
Figure 4-10 Signal purity of NO-LIF and other interference species as a function of pressure (300ppm NO seeding) for A−X(0,0) excitation. Plotted are LIF signal ratios NO/total, O₂/total and CO₂/total where total=NO+O₂+CO₂.

Figure 4-11 LIF signal purity (NO/total signal) of 300ppm NO for the A−X(0,0) excitation strategies in lean and rich flames. Different representation of data from Figure 4-10.

Again, as in the case of signal strength, the DiRosa line showed superior performance in signal purity and is highly recommended when using transitions in the A−X(0,0) band. Measurements with “DiRosa” excitation show that O₂ interference stays below 8% and that therefore a background correction is not necessary even for lean
Optimization of Excitation Strategies

(\(\phi \geq 0.83\)), high-pressure (\(p \leq 60\) bar) environments with NO concentrations of approx. 300ppm (which is comparable to concentrations present in internal combustion engines [74]).

Temperature Sensitivity using \(A-X(0,0)\) excitation

Sensitivity of the excitation lines to temperature is a key parameter when designing an experimental strategy. Quantitative NO concentration measurements without the exact knowledge of local temperature require choosing a transition which minimizes the temperature sensitivity. On the other hand, temperature sensitivity is a requirement for thermometry applications. Temperature sensitivity of all five transitions in the \(A-X(0,0)\) vibrational band is shown in Figure 4-12 for both number density and mole fractions of NO. LIF signals are proportional to the local NO number density \(N_{NO}\) (in molecules per volume), and require a conversion by a factor of \(p/kT\) to be expressed in terms of mole fractions as follows, where \(x_{NO}\) represents the mole fraction.

\[
I_{\text{LIF}} \sim N_{\text{NO}} = x_{\text{NO}} \cdot \frac{p}{kT}.
\]

The main temperature influence comes from the ground state population of the laser-coupled levels (table 4-1), broadening and shifting of absorption lineshapes, the overlap between the laser spectral profile and the spectral features of the molecule, and fluorescence yield via changes in the collisional frequencies and quenching cross-sections. The “Laurendeau” and the “DiRosa” line both cover the temperature range relevant for NO measurements in combustion systems (1250–2750 K) with less than ±10% temperature sensitivity when measuring NO concentrations. This range for the “Sick” and the “High-T” lines is shifted to the 1600–3000 K and 1750–3000 K region, respectively, and thus these lines can be useful for in-cylinder measurements in internal combustion engines. The “Low-T” line in contrast provides a technique for measuring NO at low temperatures with reduced T-sensitivity. This comparison also enables us to propose a strategy for rotational thermometry. A two-line scheme using the “DiRosa” and “High-T” lines should give high sensitivity at flame temperatures; including the
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“Low-T” line in a three-line strategy expands the temperature sensitivity range to include room temperature.

![Graph of NO LIF signal vs Temperature](image)

**Figure 4-12** Temperature dependence of the NO LIF signal with $A-X(0,0)$ excitation for constant number density (solid line) and constant mole fraction (dotted line) at $p=10$bar.

*Transmission using $A-X(0,0)$ excitation*

At the short wavelengths used here for NO detection, the transmission in high-pressure combustion environments is restricted. In our measurements near 225 nm we find that at 60 bar the laser intensity decreases by 44% over the cross section of the flame (8mm). This observation agrees well with calculations based on recently obtained absorption cross sections of hot CO$_2$ and H$_2$O [109]. For 2000 K these data predict 40% and 4% absorption by CO$_2$ and H$_2$O, respectively. Laser attenuation by NO and O$_2$ was negligible.

**4.4.2 $A-X(0,1)$ Excitation**

Three transitions which have been singled out as “promising” from the $A-X(0,1)$ band are investigated in this section. They are listed in Table 4-1 and have been given
short names, “A”, “B”, and “Jamette”. The Jamette excitation line has been previously applied in high-pressure NO-LIF measurements in the literature (referenced in Table 4-1), while the A and B lines have been newly identified using spectrally resolved 1-D line-imaging.

![Graph showing NO-LIF signal strength](image)

**Figure 4-13** Total NO-LIF signal strength in the 243–263nm bandpass region for the three $A\rightarrow X(0,1)$ candidates in $p=1$–60bar, $\phi=0.83$–1.13 flames.

**NO Signal Strength using $A\rightarrow X(0,1)$ excitation**

For NO $A\rightarrow X(0,1)$ excitation, both blue shifted (220–230nm) and red shifted detection (>240nm) strategies can be used. For comparison of signal strengths for the different transitions, Figure 4-13 shows relative NO signal strengths using a red-shifted bandpass of 243–264nm. Using blue-shifted detection results in the same relative behavior from each excitation line, but are generally lower in intensity because of the combined effects of lower Franck-Condon factors and increased absorption of the fluorescence signal. The difference between the three transitions is only minor (<15%), with the “Jamette” strategy showing the strongest signals.
Figure 4-14 Signal purity of NO-LIF and other interference species as a function of pressure (300ppm NO seeding) for $A^\prime-X(0,1)$ excitation. Plotted are LIF signal ratios NO/total, $O_2$/total and $CO_2$/total where total=$NO+O_2+CO_2$.

Figure 4-15 LIF signal purity (NO/total signal) of 300ppm NO for the $A-\chi(0,1)$ excitation strategies in lean and rich flames. Different representation of data from Figure 4-14.

**NO Signal Interference using $A-\chi(0,1)$ excitation**

Quantitative contributions of interference to the LIF signal of 300ppm NO for the different strategies for lean ($\phi=0.83$) and rich ($\phi=1.13$) flames as a function of pressure
Optimization of Excitation Strategies

(1–60bar) are shown in Figure 4-14. Three quantities plotted are overall signal purities for NO (NO/(total)), O\(_2\) (O\(_2\)/(total)) and CO\(_2\) (CO\(_2\)/(total)) where the total signal = NO+O\(_2\)+CO\(_2\). The signal purity of NO is plotted for the three transitions in Figure 4-15 for a more direct comparison. Due to lower NO signal levels in comparison to transitions in the \(A\rightarrow X(0,0)\) band, contribution of CO\(_2\) LIF plays a larger role as an interference with CO\(_2\) signal purities around 10–16% at higher pressures. Since CO\(_2\) shows a broadband absorption behavior, it is similar for all three investigated transitions. There is however a large difference between the three candidates in terms of O\(_2\) interference with the “B” candidate clearly showing the best performance in terms of interference levels. Using blue-shifted detection offers a slight improvement in the level of interference and a comparison of red and blue shifted detection strategies are addressed in Section 4.5.

![Graph](image)

**Figure 4-16** Temperature dependence of the NO LIF signal with \(A\rightarrow X(0,1)\) excitation for constant number density (solid line) and constant mole fraction (dotted line) at \(p=10\text{bar}\).

*Temperature Sensitivity using \(A\rightarrow X(0,1)\) excitation*

Temperature sensitivity of the three transitions in the \(A\rightarrow X(0,1)\) vibrational band is shown in Figure 4-16 for both number density and mole fractions of NO. The maximum NO
LIF signal is found at temperatures of 2300, 2050, and 1950K for A, B, and Jamette transitions, respectively.

**Transmission using A–X(0,1) excitation**

Transmission of the laser for excitation of A–X(0,1) is improved compared to the A–X(0,0) band since the absorption coefficient for CO$_2$ increases as the wavelength decreases. This is a major advantage for NO LIF in high-pressure environments such as internal combustion engines where post-combustion gases of both hot CO$_2$ and other absorbing hydrocarbons are present over longer distances in the propagation of the laser beam. For measurements near 235nm, we find that at 60bar the laser intensity decreases by ~24% over the cross section of the flame (6mm). A more detailed comparison between different A–X strategies is presented in Section 4.5.

**4.4.3 A–X(0,2) Excitation**

Only a single transition, “Schulz”, is investigated in the A–X(0,2) band; the choice is governed by the availability of strong KrF excimer lasers in the wavelength range of the O$_{12}$ bandhead. A detailed investigation of other transitions in the A–X(0,2) band could be carried out in the future. However, due to the very weak NO LIF intensities resulting from A–X(0,2) excitation, high power lasers are needed to produce pulses in excess of ~50mJ/pulse is required in the region of 248nm.

**NO Signal Strength and Interference using A–X(0,1) excitation**

Though a flexible choice of both blue-shifted (220–242nm) and red-shifted detection (>253nm) strategies can be used for NO A–X(0,2) excitation, the level of interference for red-shifted detection is very high due to the low population density of the $\nu''=2$ level in nominal combustion temperatures. Therefore, the only feasible detection strategy is to collect blue-shifted light below 248nm. Figure 4-17 shows relative NO signal strengths using a blue-shifted bandpass of 220–240nm. Figure 4-18 shows the interference contribution to the NO LIF by both O$_2$ and CO$_2$. Both O$_2$ and CO$_2$ LIF interference are much stronger with (0,2) excitation even with blue-shifted detection of the fluorescence signal.
Figure 4-17 Total NO-LIF signal strength in the 220−240nm bandpass region for the $A-X(0,2)$ candidate in $p=1−60$bar, $\phi=0.83−1.13$ flames.

Figure 4-18 Signal purity of NO-LIF and other interference species as a function of pressure (300ppm NO seeding) for $A-X(0,2)$ excitation. Plotted are LIF signal ratios NO/total, O$_2$/total and CO$_2$/total where total=NO+O$_2$+CO$_2$.

Detection using a narrower blue-shifted bandpass (220−240nm) can be envisioned. However, interference analysis has shown that there is negligible increase in terms of signal purity with a dramatic decrease in the signal strength (72% signal intensity
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reduction with ~1% increase in NO signal purity in a 60bar, \( \phi=0.83 \) flame). Therefore, detection of the \( A-X(0,0) \) band (220–240nm) is not recommended.

4.5 Comparison of \( A-X(0,0) \), (0,1) and (0,2) Excitation Schemes

In this section, a comparison of excitation strategies within each of the \( A-X(0,0) \), (0,1) and (0,2) bands (shown previously to yield best performance in terms of signal strength and signal interference) is presented. The transitions are “DiRosa” (0,0), “B” (0,1) and “Schulz” (0,2).

<table>
<thead>
<tr>
<th>NO ( A-X ) Band</th>
<th>(0,0) excitation</th>
<th>(0,1) excitation</th>
<th>(0,1) excitation</th>
<th>(0,2) excitation</th>
<th>(0,2) excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0,1)+(0,2) detection</td>
<td>(0,0) detection</td>
<td>(0,2)+(0,3) detection</td>
<td>(0,0)+(0,1) detection</td>
<td>(0,3)+(0,4) detection</td>
</tr>
</tbody>
</table>

Excitation and Detection Strategy (nm)

<table>
<thead>
<tr>
<th>Excitation at 1bar Detection</th>
<th>226.031 nm</th>
<th>235.870 nm</th>
<th>235.870 nm</th>
<th>247.941 nm</th>
<th>247.941 nm</th>
</tr>
</thead>
</table>

Relative Signal Strengths at 10bar (60bar)

| Experimental \( \phi=0.83 \) | 100 (100) | 18 (17) | 42 (39) | 4.1 (3.4) | 2.3 (1.9) |
| Simulated \( T=1900K \)      | 100 (100) | 15 (14) | 28 (26) | 3.1 (3.1) | 1.3 (1.4) |

Table 4-2 Results of the Analysis for the Different Excitation and Detection Strategies: Comparison of Signal Strengths.

The discussion now includes the influence of detection bandpass (red-shifted or blue-shifted), yielding a total of five excitation-detection strategies as defined in the top row of Table 4-2. The comparison also includes calculated laser and signal absorption at the involved wavelengths, and temperature and pressure dependence of the LIF signals.

4.5.1 Signal Strength in Nonabsorbing Environments

In order to maximize signal strength, an NO transition with a large ground state population at flame temperatures and high oscillator strength should be chosen. At
typical combustion temperatures of 1500–2500K, largest vibrational population is present in the $X$, $v'' = 0$ state. The $v'' = 1$ and 2 states have respective energies of 1846 and 3724 cm$^{-1}$ above the ground state [85], corresponding to maximum populations at ~2700 and ~5400K, respectively. Largest lower state populations are therefore found in the $A-X(0,0)$ band in most combustion applications. Slightly higher oscillator strengths of the (0,1) and (0,2) bands (factor of 1.4 and 1.1 higher than the (0,0) strength, respectively) cannot compensate for the lower population.

![Diagram of signal strengths](image)

**Figure 4-19** Calculated and experimental signal strengths for the 10 bar flame for the excited (exc.) and detected (det.) vibrational bands within the NO $A-X$ system.

Figure 4-19 shows measured and simulated signal strengths for the different $A-X$ strategies for excitation in a 10 bar flame, normalized to the signal strength of the (0,0) approach. The results are summarized in Table 4-2 which also gives the data for 60 bar flames. The simulations have been performed for a typical flame temperature of 1900 K [116]. It should be noted that the experimental values are not directly comparable between the different vibrational bands because of the different dye laser configurations necessary for the different wavelengths; qualitatively, the experimental and simulated signal strengths agree well. $A-X(0,0)$ strategies clearly show the strongest signals, $A-X(0,1)$ excitation yields signal intensities about an order of magnitude lower. Signal is
decreased by another order of magnitude with $A-X(0,2)$ excitation. The difference between red- and blue-shifted detection reflects the different Franck-Condon emission factors.

Considering signal strength alone, $(0,0)$ excitation is clearly the strategy of choice. However, in the hot post-flame combustion gas where absorption coefficients are strongly wavelength-dependent, the other strategies should not be discarded simply on the basis of signal strength. This is discussed in the next subsection. Furthermore, the high laser power of the tunable excimer laser usually used for $(0,2)$ excitation may partially compensate for the low signal strength for imaging measurements where the output of dye lasers limits the excitation energy for the laser sheet.

### 4.5.2 Influence of Attenuation by Hot CO$_2$ and H$_2$O

Hot combustion products like CO$_2$ and H$_2$O have long been ignored as potential absorbers in laser-based combustion diagnostic work. However, at wavelengths shorter than 250nm for CO$_2$ and shorter than 230nm for H$_2$O their influence becomes important and increases towards shorter wavelengths [109, 118]. This causes attenuation of the laser as well as the fluorescence light. The transmission depends not only on the wavelength, but also on the path length and therefore on flame geometry and experimental configuration. This produces nearly opposite effects: With $(0,0)$ excitation and red-shifted detection, strong laser attenuation but weak signal attenuation occurs; with $(0,2)$ excitation and blue-shifted detection, laser attenuation is weak but signal attenuation is stronger. For a quantitative comparison, laser and signal transmission are calculated for flame center positions in two typical high-pressure flame configurations:

**Case 1.** Stanford high-pressure burner, 40bar, 1900K, 8 mm diameter  
**Case 2.** DI Diesel engine, 50bar, 2400K, 80 mm diameter, laser travels through cylinder window, detection through piston window (e.g., Ref. [76])

The calculations are performed using the expressions given by Schulz et al. [109] for $\phi=0.9$ equilibrium exhaust gas concentrations of CO$_2$ and H$_2$O. The results are given in Table 4-3. The different influence of laser and signal wavelengths can clearly be
followed.

<table>
<thead>
<tr>
<th>NO $A-X$ Band</th>
<th>(0,0) excitation</th>
<th>(0,1) excitation</th>
<th>(0,1) excitation</th>
<th>(0,2) excitation</th>
<th>(0,2) excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>detection</td>
<td>(0,1)+(0,2)</td>
<td>(0,0)</td>
<td>(0,2)+(0,3)</td>
<td>(0,0)+(0,1)</td>
<td>(0,3)-(0,4)</td>
</tr>
</tbody>
</table>

### Transmission for High-Pressure Burner, 40bar, 1900K

| Laser     | 82 % | 89 % | 89 % | 95 % | 95 % |
| Signal    | 92 % | 81 % | 95 % | 87 % | 98 % |
| Total     | 75 % | 73 % | 85 % | 82 % | 92 % |
| Signal Strength | 75 | 11 | 24 | 2.5 | 1.2 |

### Diesel Engine, 50bar, 2400K

| Laser     | 0.48 % | 4.0 % | 4.0 % | 17 % | 17 % |
| Signal    | 53 %   | 26 %  | 67 %  | 38 % | 80 % |
| Total     | 0.25 % | 1.0 % | 2.7 % | 6.4 % | 13 % |
| Signal Strength | 0.25 | 0.16 | 0.77 | 0.20 | 0.18 |

**Table 4-3** Results of the Analysis for the Different Excitation and Detection Strategies: Calculated Transmission Properties of CO$_2$ and H$_2$O Exhaust for Two Practical Situations

In case 1, the high-pressure flame, total transmission (laser and signal) varies between 75 and 92% for the investigated strategies, but the difference between (0,0) excitation/(0,1),(0,2) detection and (0,2) excitation/(0,0),(0,1) detection is small (75% vs. 82% total transmission). In case 2, the Diesel engine, absorption is much stronger because of the higher temperatures and longer paths involved. In this geometry with long laser path and short signal path (detection through piston window), (0,0) excitation has a strong disadvantage. In this case there is a large difference when comparing (0,0) excitation/(0,1),(0,2) detection and (0,2) excitation/(0,0),(0,1) detection, the latter strategy yielding a total transmission of 26 times that of the former. Table 4-3 also gives relative signal strengths, normalized to the signal strength of the (0,0) strategy without absorption.
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Figure 4-20 Calculated signal strengths after laser and signal absorption by hot CO$_2$ and H$_2$O, normalized to the (0,0) strategy signal without absorption for the excited (exc.) and detected (det.) vibrational bands within the NO $A-X$ system.

This data are also shown in Figure 4-20. In the high-pressure flame the strong difference in signal strength in non-absorbing environments persists; however, in the Diesel engine signal strengths are all within the same order of magnitude. Longer-wavelength excitation should be preferred here because the overall larger transmission is much larger and signals are therefore less influenced by fluctuations of pressure or temperature.

It is important to emphasize that the transmission properties strongly depend on the specific combustion situation (pressure, temperature) and experimental geometry (laser and signal paths). In internal combustion engines, for example, signal transmission may increase, decrease or stay constant with piston position due to the simultaneous variation of pressure, temperature, and path length, depending on the position of the laser beam above the piston window. The advantage of long-wavelength excitation is most pronounced at very high pressure (above ca. 40 bar) and long laser path lengths. Therefore, an understanding of combustion conditions and relevant geometries is required for selection of an appropriate excitation and detection strategy.
**Figure 4-21** Purity of the LIF signals for NO, O\(_2\) and CO\(_2\) with 300ppm NO for different excitation and detection strategies in lean and rich flames. Plotted are signal purity for NO (NO/total), O\(_2\) (O\(_2\)/total) and CO\(_2\) (CO\(_2\)/total) where total=NO+O\(_2\)+CO\(_2\). Excitation within (0,0), (0,1) and (0,2) bands is performed at 226.03 ("Dirosa"), 235.87 ("B") and 247.94nm ("Schulz"), respectively.

4.5.3 Signal Interference

Figure 4-21 shows the contribution of interference to the LIF signal of 300ppm NO for the different strategies for lean (φ=0.83) and rich (φ=1.13) flames with pressures between 1 and 60bar; these results are also summarized in Table 4-4 for 10 and 60bar. Plotted in
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Figure 4-21 are the quantified LIF signal purities of NO (NO/total), O₂/NO (O₂/total) and CO₂ (CO₂/total) where total=(NO + O₂ + CO₂) for the three representative transitions in the A−X(0,0), (0,1) and (0,2) bands of NO.

<table>
<thead>
<tr>
<th>NO A–X Band</th>
<th>(0,0) excitation (0,1)+ (0,2) detection</th>
<th>(0,1) excitation (0,0) detection</th>
<th>(0,1) excitation (0,2)+(0,3) detection</th>
<th>(0,2) excitation (0,0)+(0,1) detection</th>
<th>(0,2) excitation (0,3)+ (0,4) detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂/total</td>
<td>.9% (13%)</td>
<td>5.4% (16%)</td>
<td>2.4% (16%)</td>
<td>2.2% (20%)</td>
<td>4.3% (16%)</td>
</tr>
<tr>
<td>CO₂/total</td>
<td>0% (7.1%)</td>
<td>0.3% (10%)</td>
<td>.6% (16%)</td>
<td>4.3% (35%)</td>
<td>19% (68%)</td>
</tr>
<tr>
<td>NO/total</td>
<td>99% (80%)</td>
<td>94% (73%)</td>
<td>97% (68%)</td>
<td>94% (45%)</td>
<td>77% (16%)</td>
</tr>
</tbody>
</table>

Table 4-4 Results of the Analysis for the different excitation and detection Strategies: LIF Signal Interference Relative to the LIF Signal of 300ppm NO at 10bar (60bar) (%)

As previous mentioned, the interference strongly increases with pressure. NO emission gets weaker with increasing pressure due to pressure broadening leading to a decrease in excitation efficiency, whereas the effects of fluorescence quantum yield and NO number density cancel for constant mole fraction. O₂ and CO₂ emission increases linearly with pressure due to the increase in number density, while their fluorescence quantum yields stay approximately constant.

O₂-LIF is the main source of interference in lean flames. Its LIF contribution can easily reach 20% of the NO signal in the lean 60bar flame investigated here. The O₂ LIF interference increases in the order of (0,0), (0,1) and (0,2) excitation. With (0,1) excitation there is essentially no difference between red- or blue-shifted detection; with (0,2) excitation blue-shifted detection suppresses O₂ LIF signal by a factor of two in comparison to red-shifted detection. CO₂ LIF is important in both lean and rich flames,
especially if a broad detection bandpass is used. Its relative contribution is strongly increasing in the order of (0,0) and (0,1) excitation and is the dominant source of interference with (0,2) excitation. It is generally much stronger with red-shifted detection in comparison with blue-shifted detection.

The signal purity (NO/total emission) is the most relevant parameter for practical imaging application, since it is the direct measure of how much of the detected signal is due to NO. From Figure 4-21, it can be seen that it decreases almost linearly with pressure for all investigated strategies. It is also generally lower in lean flames than in rich flames due to both higher O\textsubscript{2} and CO\textsubscript{2} interference. The (0,0) excitation strategy is the best choice for highest signal purities; (0,1) strategies with both red- and blue-shifted detection yield only slightly lower purities. With (0,2) excitation blue-shifted detection shows a much better performance than red-shifted detection; still, signal purity may become as low as 50% in the lean 60 bar flame.

The discussion so far was based on the results of the seeded laminar high-pressure burner (LIF signal of 300 ppm NO). In internal combustion engines, NO concentrations may be much higher (>1000 ppm), while in unseeded high-pressure burners NO concentration are often much lower (<100 ppm). The importance of signal interference therefore strongly depends on the particular combustion situation. Note that the measurements in modestly rich (\(\phi<1.2\)) premixed flames avoid the potential PAH interference in very rich or non-premixed combustion environments. The assessment of PAH interference is beyond the scope of this work.

4.5.4 Temperature and Pressure Dependence

Temperature Dependence
Quantitative NO concentration measurements without the exact knowledge of local temperature require choosing a transition which minimizes the temperature sensitivity. The main temperature influence of NO-LIF signal strength (on a per-molecule basis) arises from the ground state population of the laser-coupled levels. Since line broadening and -shifting is temperature dependent, the overlap of the spectral features with the spectral shape of the laser also shows temperature dependence. Temperature furthermore
influences the fluorescence quantum yield by changing collisional frequencies and quenching cross-sections. The combined temperature effects of ground state population, spectral overlap and quantum yield were calculated for the different strategies in the 10bar flame with 0.4cm\(^{-1}\) laser FWHM based on a non-transient three-level NO LIF model (LIFSim [10]).

**Figure 4-22** Simulated temperature dependence of the NO-LIF signal for number density and mole fraction (signal interpretation on a per-molecule and a per-volume basis). The simulations are performed for \( p=10\text{bar} \), \( T=1900\text{K} \), with the laser tuned to a constant excitation wavelength corresponding to the NO peak at 10bar.

Figure 4-22 shows and compares the temperature sensitivity of LIF intensities for NO number density and mole fraction measurements (number density = mole fraction × \( P/kT \)). The data are also given in Table 4-5. For number density measurements, the LIF signal yield is relatively independent of temperature for \( A−X(0,0) \) excitation strategies. Due to the large ground state energies of \( A−X(0,1) \) and \( (0,2) \) transitions, the maximum LIF signal is found at high temperatures of 2815K for the \( (0,1) \) strategy and 3770K for the \( (0,2) \) strategy, and signals are strongly decreasing towards lower temperatures. Correction for this temperature effect is necessary for interpretation of the LIF signal
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when measuring NO number densities. On a per-volume basis, relevant when measuring mole fractions, temperature sensitivity is most pronounced for (0,0) excitation, where the signal continually decreases above 1000K. With (0,1) and (0,2) excitation least temperature sensitivity is found around 2055 and 2715K, respectively. Mole fractions are therefore best derived from experiments with (0,1) or (0,2) excitation for minimum temperature sensitivity.

<table>
<thead>
<tr>
<th>NO $A-X$ Band</th>
<th>Excitation</th>
<th>Detection</th>
<th>Temperature of maximum LIF signal</th>
<th>Signal variation for 1700−2500K</th>
<th>Temperature of maximum LIF signal</th>
<th>Signal variation for 1500−2500K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0,0)</td>
<td></td>
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<tr>
<td>number density measurement</td>
<td>(0,1)+(0,2)</td>
<td>(0,0)</td>
<td>1645 K</td>
<td>+/- 6.8 %</td>
<td>&lt; 1000 K</td>
<td>+/- 25 %</td>
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<tr>
<td>mole fraction measurement</td>
<td>(0,1)</td>
<td>(0,0)</td>
<td>2815 K</td>
<td>+/- 18 %</td>
<td>2055 K</td>
<td>+/- 3.1 %</td>
</tr>
<tr>
<td></td>
<td>(0,1)</td>
<td>(0,2)+(0,3)</td>
<td>2815 K</td>
<td>+/- 18 %</td>
<td>2055 K</td>
<td>+/- 3.1 %</td>
</tr>
<tr>
<td></td>
<td>(0,2)</td>
<td>(0,0)+(0,1)</td>
<td>3770 K</td>
<td>+/- 36 %</td>
<td>2715 K</td>
<td>+/- 19 %</td>
</tr>
<tr>
<td></td>
<td>(0,2)</td>
<td>(0,3)-(0,4)</td>
<td>3770 K</td>
<td>+/- 36 %</td>
<td>2715 K</td>
<td>+/- 19 %</td>
</tr>
</tbody>
</table>

Table 4-5 Results of the analysis for the different excitation and detection strategies: simulated temperature dependence at 10bar.

Table 4-5 also gives the magnitude of the LIF signal variation between 1700 and 2500K. This corresponds to the systematic error that is induced in NO concentration measurements at these temperatures typical for high-pressure combustion situations when no temperature information is available for correction of the LIF signals. For number density measurements, the (0,0) approach yields the least temperature variation of +/-7 % (relative to the average signal). For mole fraction measurements, the (0,1) approach yields a temperature variation of only +/-3 %. If local temperature is not known, these strategies should be chosen to minimize systematic errors, depending on the choice of measured quantity.
Chapter 4

Pressure Dependence

The LIF signal depends on pressure through the change in excitation efficiency (line broadening and -shifting) and fluorescence quantum yield (quenching). The overall effect leads to a strong nonlinear decrease in LIF signal with pressure. The simulated pressure dependence of the NO LIF signal for constant number density (corresponding to the signal strength on a per-molecule base) is shown in the left panel of Figure 4-23 for the three excitation strategies. The LIF signal strength decreases by more than two orders of magnitude between 1 and 40bar. In practice this decrease is partly compensated by the effect of increasing number density with pressure, leading to strong LIF signals even at elevated pressures.

![Figure 4-23](image)

**Figure 4-23** Simulated pressure dependence of the NO-LIF signal for number density and mole fraction measurement, normalized to the 10bar value. The laser is tuned to a constant excitation wavelength corresponding to the NO peak at 10bar.

When LIF measurements are performed to quantify mole fractions, quenching (which is \( \sim p \) and therefore decreases the fluorescence quantum yield \( \sim 1/p \)) cancels with the pressure dependence of number density (which is also \( \sim p \), cf. eq. (4.1)). The variation of signal with pressure then only depends on the pressure-dependent spectral overlap between laser and absorption feature. The resulting simulated signal strengths are shown in the right panel of Figure 4-23. This data corresponds to the pressure dependence of the overlap fraction, i.e., the absorption efficiency. Because of the particular shape of the absorption feature and the density of transitions nearby, the pressure dependence varies slightly for the different excitation approaches. It is interesting to note that above ca.

94
50bar absorption efficiency does not change any more; instead, all rotational lines of the vibrational band are completely merged by pressure broadening. In practice, pressure is readily measured in most static and fluctuating combustion situations, and pressure effects can relatively easily be accounted for.

### 4.6 Conclusion

Laser-induced fluorescence measurements and LIF simulation calculations were used to evaluate the performance of selected transitions in the $A−X(0,0)$, $(0,1)$ and $(0,2)$ bands of NO. Experiments were carried out in laminar, premixed methane/air flames between 1 and 60bar with equivalence ratios between $\phi=0.83$ and 1.13. In total, nine individual rovibrational transitions from the $A−X(0,0)$, $(0,1)$ and $(0,2)$ bands were examined. Different excitation strategies were compared within each vibrational band and across the different $A−X$ bands. The following is a comprehensive evaluation from the results in this chapter.

#### $A−X(0,0)$ Excitation

- The $A−X(0,0)$ approach offers the strongest signals due to the high density of the ground state population at combustion temperatures.
- The “DiRosa” excitation line at 226.03nm offers the best performance in terms of both signal strength and suppression of interference from $O_2$. (signal purity $\geq$80% for $\phi=0.83$, 60bar flame)
- The “High-T” excitation line at 224.82nm offers good signal purity ($\geq$68% for all flame conditions) with high ground state energy (1750–4032K), and the “Low-T” excitation line at 226.87nm offers reasonable spectral purity (63% for all flame conditions) with low ground state energy (178–232K). Along with the “DiRosa” line, two or three line thermometry can be achieved.
- Attenuation of the probe beam is the highest among the $A−X$ excitation strategies, and therefore suitable for probe volumes with small laser path requirements.
- Only red-shifted detection is possible, where strong interference from $O_2$, CO$_2$ and PAH can cause problems.
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\( A-X(0,1) \) Excitation

- The \( A-X (0,1) \) approach offers relatively strong signals (approximately one third of the \((0,0)) \) and at the same time reduces attenuation of both laser and signal light (red-shifted detection).
- The “Jamette” excitation line at 236.22nm shows the highest signal strength and is suitable for environments with very little \( O_2 \). However, this transition suffers from high levels of interference of \( O_2 \) LIF with signal purities as low as 55% for red shifted detection in a \( \phi=0.83 \), 60bar flame.
- The “B” excitation line at 235.87nm is very promising, offering high signal purities (≥68% for all flame conditions) and sufficient signal intensity.
- Blue-shifted detection for \( A-X(0,1) \) excitation offers no particular advantage in signal strength, signal purity or transmission properties. However, this may change in the presence of PAH. In addition, attenuation of the fluorescence signal when using blue-shifted detection is strong due to the short wavelength (~226nm).
- Minimum temperature sensitivity of ground state population at flame temperature, which enables concentration measurements without detailed knowledge of temperatures.

\( A-X(0,2) \) Excitation

- Blue-shifted detection is preferred since red-shifted detection suffers from strong interference and generally is not recommended.
- The \( A-X (0,2) \) approach offers minimum absorption of laser radiation in combustion environments, and is suitable for geometries with long laser path and short signal path (due to short wavelength of the signal light).
- Signal levels are weak due to low population of the vibrational ground state. Lasers with higher intensity are required.
- There is a strong temperature dependence of the ground state population, requiring accurate temperature information for correcting the LIF signal intensity. This characteristic can be an advantage when using the transition for thermometry applications.
Optimization of Excitation Strategies

- Effective for suppression of PAH interference.

All three $A-X$ vibrational transitions have advantages and disadvantages depending on the experimental condition. The choice of the excitation strategy depends on the specific combustion environment, geometry of the combustion chamber, availability of laser equipment and an understanding of the global chemistry involved in the reaction (i.e., understanding of fuel and oxidizer, equivalence ratio and major byproducts from the combustion process).
Chapter 5 High Pressure CO$_2$ UV LIF

In this chapter, laser-induced fluorescence (LIF) of carbon dioxide (CO$_2$) using UV excitation is presented. CO$_2$-LIF in this wavelength region is of significant importance as the excitation-emission of CO$_2$ overlaps with the $\gamma$ bands of NO and influences the evaluation of NO-LIF intensities. The CO$_2$-LIF signal consists of a broad (200−450nm) continuum with a faint superimposed structure, and was identified for the first time while conducting NO-LIF research presented in this thesis. CO$_2$-LIF is investigated with excitation between 215 and 255nm with spectrally resolved detection in 5−40bar premixed CH$_4$/O$_2$/Ar and CH$_4$/air flat-flames at fuel/air ratios between 0.8 and 1.9. The CO$_2$-LIF signal is linear with pressure and laser fluence within the investigated ranges, potentially showing promise as a new diagnostics tool. As a demonstration, semi-quantitative CO$_2$ PLIF images in high-pressure CH$_4$/air flames (10−60bar) are presented. A portion of the work presented in this section has been conducted in collaboration with University of Heidelberg [114].

5.1 Background

The identification of CO$_2$-LIF was motivated by two main observations, which impacted the interpretation of signals during high-pressure NO-LIF.

The first observation was the attenuation of laser and signal light in this spectra range for practical high-pressure applications. Figure 5-1 (lower left panel) shows raw signals obtained using NO PLIF in a 60bar, $\phi$=0.9 flame with an excitation wavelength of 226.03nm. As can be seen from the figure, there is severe attenuation of the LIF intensity along the path of the laser beam. The profile of the intensity is plotted in Figure 5-1 (lower right panel) as a function of distance for clarity. Despite the small size of the flame (8mm exit diameter), the total reduction in the LIF signal was up to 43% at 60bar...
for the combination of 226nm excitation and detection at 237nm (10nm spectral detection width). From a practical point of view, this effect results in transmission problems of the probe beam (laser) as well as uneven attenuation of the fluorescence signal.

Figure 5-1 Raw PLIF image of NO in a $\phi=0.9$, 60bar CH\textsubscript{4}/air flame (lower left panel). The attenuation profile between the two black lines in the left image is plotted as function of distance (lower right panel).

It was not until recently that the main absorbing species responsible for the attenuation were identified as hot, vibrationally excited carbon dioxide (CO\textsubscript{2}) and water (H\textsubscript{2}O). Schulz et al., measured UV absorption cross-sections between 190 and 320nm of shock-heated CO\textsubscript{2} between 880 and 3050K and H\textsubscript{2}O between 1230 and 2860K [109, 110], and found that attenuation corrections could be made in practical high-pressure applications using the newly acquired absorption data. It was also shown that for the relevant temperatures (~2000K) and wavelength ranges (200–300nm) used in the NO-LIF research, CO\textsubscript{2} was the dominant species for this effect. CO\textsubscript{2}, while transparent in the ultraviolet (UV) at wavelengths longer than 205nm, dramatically increases in absorption
capacity at temperatures above 1000K. An example of measured CO$_2$ optical absorption cross-section versus wavelength for five temperatures (940, 1160, 1630, 2310 and 3050K) is shown in Figure 5-2. The full data set can be represented by a numerical fit for cross-section $\sigma$ in the range 200–320nm and 900–3050K using a semi-empirical form: 

$$\ln \sigma_{CO_2}(\lambda,T) = a + b \lambda, \text{ where } a = c_1 + c_2 T + c_3 / T \text{ and } b = d_1 + d_2 T + d_3 / T.$$ 

The cross-section is given in units $10^{-19}\text{ cm}^2$ with $T$, in 1000K, $\lambda$, in 100nm, and $c_1=17.2456$, $c_2=-3.1813$, $c_3=0.8836$, $d_1=-7.0094$, $d_2=1.6142$, and $d_3=-3.1777$ [110].

**Figure 5-2** CO$_2$ optical absorption cross-section versus wavelength for 5 temperatures (940, 1160, 1630, 2310 and 3050K) measured in shock heated CO$_2$/Ar mixtures.

Observation of such pronounced attenuation from CO$_2$ raised the question of the fate of the excited CO$_2$ via absorption and the possibility of potential de-excitation channels via spontaneous emission, and became a motivation for the study of CO$_2$-LIF. As an added note, the degree of attenuation can itself be used as a diagnostics tool for temperature measurements in uniform distributions of CO$_2$: demonstrations of thermometry based on CO$_2$ absorption for various applications were reported in a recent publication by Jeffries et al. [119].

The second observation that motivated this study was the pervasive broadband-emission that overlaps with the $\gamma$ bands of NO and Schumann-Runge bands of O$_2$ (200–450nm) in spectrally resolved 1-D line-imaging. The broad continuum structure
became more evident when exciting NO with longer wavelengths (e.g., $A-X(0,1)$ and more so with $A-X(0,2)$), as relative NO LIF intensities were reduced. An example of this emission is shown in Figure 5-3 where, a broad baseline extends from 200nm and up.

![Figure 5-3](image)

**Figure 5-3** Emission Spectra of NO-LIF using 226.03nm Excitation in a $\phi$=0.9, 40bar flame, 300ppm NO seeding). Broadband emission evident throughout the entire region.

The broadband signal received attention because it proved to be a significant source of interference in detection of NO-LIF, especially when applying red-shifted detection with either $A-X(0,1)$ or $A-X(0,2)$, with CO$_2$ signal fractions of 16% and 68%, respectively when using a red-shifted 20nm detection bandwidth at 60bar (Chapter 4). In addition, the broadband signal was required as a key component in numerically separating the emission spectra into the different spectral components (as in Figure 5-3). In this chapter, strong evidence is presented that this signal arises from CO$_2$, as the signal variations with excitation wavelength, equivalence ratio and flame temperature all correlate with CO$_2$ absorption cross-sections. Laser-induced fluorescence of CO$_2$ was identified by systematic studies of spectrally resolved 1-D line-imaging measurements in high-pressure methane flames at pressures up to 40bar. To separate the broadband CO$_2$-LIF signal from signal contributions of other species, nitrogen-free flames (diluted with Ar) were primarily used for the measurements. LIF of hot O$_2$ was minimized by tuning
the laser wavelength to minima in the O\textsubscript{2} absorption spectrum. H\textsubscript{2}/O\textsubscript{2}/Ar flames were investigated to demonstrate the absence of the broadband emission signal attributed to CO\textsubscript{2}.

From a practical perspective, the intensity of CO\textsubscript{2} fluorescence is comparable to or greater than the signal intensity of NO-LIF depending on the excitation and detection strategy used. In addition, the use of CO\textsubscript{2}-LIF as a diagnostic tool is proposed by a demonstration of semi-quantitative CO\textsubscript{2} PLIF imaging in high-pressure CH\textsubscript{4}/air flames.

5.2 Experimental

Experiments were conducted in the Stanford high-pressure burner previously described in Section 3.1. Laminar, premixed CH\textsubscript{4}/air, CH\textsubscript{4}/O\textsubscript{2}/Ar and H\textsubscript{2}/O\textsubscript{2}/Ar flat-flames at pressures from 1 to 40bar were investigated for fuel/air equivalence ratios of φ=0.8–1.9. The soot limit was found between φ=1.6 and 1.7 for the CH\textsubscript{4}/O\textsubscript{2}/Ar flame at 20bar.

A Nd:YAG-pumped (Quanta Ray GCR250) frequency-doubled (BBO) dye laser (LAS, LDL205) was used to produce laser light (ca. 1mJ, 0.4cm\textsuperscript{-1} full-width at half maximum, FWHM). The laser was tuned to different excitation wavelengths, which were selected from O\textsubscript{2}-LIF simulations (LIFSim, [10]) for minimum O\textsubscript{2}-LIF interference. The laser was scanned in a ±0.5nm range around the simulated O\textsubscript{2} minima for experimental confirmation of the O\textsubscript{2} excitation spectra. Three different laser dyes were necessary to cover the broad excitation wavelength range of 40nm. Measurements were carried out at 215.70, 220.88, and 226.07nm (Coumarin 120); 233.65, 235.88, and 242.15nm (Coumarin 102); 247.95, 251.69, and 255.88nm (Coumarin 307). The laser beam quality changes slightly within the investigated wavelength range. Therefore, O\textsubscript{2}-Raman signals and their known wavelength dependence are measured in the cold fresh gas and were used as an internal reference.

The laser beam was aligned parallel to the burner surface and passed through the center of the flame 2mm above the burner matrix in a 1-D line-imaging setup (Figure 3-8). The pulse energy was measured with a fast photodiode (LaVision). The beam was
mildly focused with a spherical lens \((f=700\text{mm})\), and the measurement occurs in the beam waist. Fluorescence signals were collected at right angles to the laser beam and focused with a \(f=105\text{mm}\), \(f'_\#=4.5\) achromatic UV lens (Nikon) onto the horizontal entrance slit of a \(f=250\text{mm}\) imaging spectrometer (Chromex 250IS, 300 grooves/mm grating, blazed for 300nm operated in first order). Narrowband dielectric mirrors (FWHM \(~15\text{nm}\)) were used to suppress elastically scattered laser light. The spectrally dispersed signal was detected with an intensified CCD camera (LaVision, FlameStar III).

Corrections to the signal for spectral response of the filter, spectrometer and camera were made using calibration measurements with a calibrated D\(_2\)-lamp (Optronics Laboratories Inc.). In order to compare signal intensities for different wavelength excitation (with slight variations in beam quality and beam alignment), O\(_2\) Raman scattering intensities at 20 bar in the cold coflow region were used as an internal reference while accounting for the wavelength-dependence of Raman cross-sections. CO\(_2\) LIF signals were averaged on the spectral axis to simulate different detection bandpass filters (280–320nm and 320–370nm, respectively). In lean flames O\(_2\) LIF contributes to the signal transmitted by the shorter-wavelength bandpass.

### 5.3 Investigation of CO\(_2\) LIF

Identification process of CO\(_2\)-LIF and relevant spectroscopy is presented in this section. In addition, the effect of CO\(_2\) LIF as a major source of interference source in NO-LIF diagnostics is discussed.

#### 5.3.1 Spectrally resolved 1-D line-Imaging

Spectrally resolved 1-D line-imaging allows quantitative study of the broadband emission and probing of its dependence on experimental conditions. In high-pressure flames, pressure-induced line broadening makes it difficult to completely avoid the fluorescence from alternatively excited species such as NO or hot O\(_2\) by tuning the laser wavelength off-resonance. Therefore, measurements were made by eliminating nitrogen from the flame by using oxygen diluted in argon (20/80 volume ratio; note this dilution
High Pressure CO\textsubscript{2} UV LIF

retains a similar heat capacity and thus similar flame temperatures) instead of air. Effectively, this also allows the elimination of a nitrogen-containing species as a possible candidate of the broadband emission. The excitation wavelengths were selected to minimize oxygen excitation and measurements were made over a wide equivalence ratio ($\phi$=0.8–1.8). An example of the emission spectra for the different equivalence ratios using 226nm excitation are shown in Figure 5-4.

![Emission spectra for different equivalence ratios in a CH\textsubscript{4}/Ar/O\textsubscript{2} flame at 20bar for excitation wavelength 226.1 and 235.9nm.](image)

**Figure 5-4** Emission spectra for different equivalence ratios in a CH\textsubscript{4}/Ar/O\textsubscript{2} flame at 20bar for excitation wavelength 226.1 and 235.9nm.

Even with active suppression (by selection of optimized excitation wavelength), O\textsubscript{2} LIF dominates the emission spectrum in lean and stoichiometric flames at high pressure (Figure 5-4, $\phi$=0.8). Underlying the oxygen spectrum is a broad-band background that can be observed without O\textsubscript{2}-LIF contribution in the fuel rich ($\phi$=1.1 and 1.5) flames. This signal is attributed to CO\textsubscript{2} LIF. In the very rich flame ($\phi$=1.8) an additional strong signal from soot precursors (polycyclic aromatic hydrocarbons, PAH) is observed which has a qualitatively different spectral shape. The PAH-LIF spectra have a maximum at longer wavelengths relative to the broadband CO\textsubscript{2}-LIF emission spectrum. It is interesting to note that among the different excitation wavelengths used, the lower three (<226nm) showed very little emission from PAH as can be seen from Figure 5-4 (right panel). As a part of the identification process, a high-pressure H\textsubscript{2}/O\textsubscript{2}/Ar flame was
stabilized to check for the broadband emission. Since the post-combustion gases of a H$_2$/O$_2$/Ar flame is mainly water with no carbon containing compound, the broadband signal was expected to disappear completely. A confirmation of this is shown in Figure 5-5.

![Emission spectra with 235.88-nm excitation in a CH$_4$/O$_2$/Ar (upper trace) and a H$_2$/O$_2$/Ar (lower trace) flame (20 bar, φ=1.1). Note the peak near 260 nm in the H$_2$/O$_2$/Ar flame corresponds to Raman scattering from H$_2$O.](image)

**Figure 5-5**

5.3.2 CO$_2$ LIF Intensity Dependence

To assure the assignment of the broadband fluorescence as CO$_2$ LIF, the signal dependence on CO$_2$ concentration, temperature, and excitation wavelength is investigated and compared to the variation expected from the recently determined CO$_2$ absorption cross-sections [110]. For quantification of the CO$_2$ fluorescence intensity, profiles of the broadband emission features were extracted by taking emission spectra of the CH$_4$/O$_2$/Ar flame at 20 bar, φ=1.1 for each excitation wavelength. The Rayleigh peak was cut out and the resulting emission was fit using a modified peak function,
High Pressure CO$\textsubscript{2}$ UV LIF

\[ y = A \times \exp(-\exp(-(x - x_c)/2) - (x - x_c)/w + 1) + B \times (x - x_c)^2 / 10^4, \quad (5.1) \]

where \( A \), \( x_c \), and \( w \) are the fit parameters. An example of this fitting for an excitation wavelength of 226nm is shown in Figure 5-6. The fit represents the emission well, and is used to evaluate the intensity of the CO$\textsubscript{2}$ emission using specific detection bandpass. Experiments have shown that the maximum of the emission shifts slightly with excitation wavelength.

\[ y = A \times \exp(-\exp(-(x - x_c)/w) - (x - x_c)/w + 1) + B \times (x - x_c)^2 / 10^4 \]

\[ \begin{array}{ll}
\text{Chi}^2 & = 81.72231 \\
R^2 & = 0.87485 \\
A & = 92.82509 \pm 5.22985 \\
x_c & = 255.05917 \pm 1.32121 \\
w & = 41.00135 \pm 3.98335 \\
B & = 4.27831 \pm 11.03566 \\
xc2 & = 152.28437 \pm 9.11149 \\
\end{array} \]

\[ y = A \times \exp(-\exp(-(x - x_c)/w) - (x - x_c)/w + 1) + B \times (x - x_c)^2 / 10^4 \]

\[ \begin{array}{ll}
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\[ y = A \times \exp(-\exp(-(x - x_c)/w) - (x - x_c)/w + 1) + B \times (x - x_c)^2 / 10^4 \]

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w & = 41.00135 \pm 3.98335 \\
B & = 4.27831 \pm 11.03566 \\
xc2 & = 152.28437 \pm 9.11149 \\
\end{array} \]

**Figure 5-6** Determination of the CO$\textsubscript{2}$-LIF emission profile by numerical fitting of a \( \phi = 1.1 \), 20 bar CH$\textsubscript{4}$/Ar/O$\textsubscript{2}$ flame using a modified peak function.

The CO$\textsubscript{2}$-fluorescence signal is strongly dependent on excitation wavelength. This is shown in Figure 5-7 in which the integrated LIF is shown as a function of wavelength for various detection wavelength in a 20 bar, \( \phi = 1.1 \) flame. Three detection bands are used: 320–370nm (square marker) for minimum interference in lean flames, 280–320nm (round marker) which is just red-shifted of the Rayleigh peak, and a relative bandpass from +10 to +60nm red-shifted of the excitation wavelength (triangle). The relative bandpass was used since the emission maximum shifts slightly with excitation wavelength. The trend of change in the LIF intensity is in qualitative agreement with the
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wavelength dependence of the CO$_2$ absorption cross-section. A 0$^\text{th}$-order assumption that the fluorescence quantum yield is independent of temperature and that the CO$_2$-LIF signal is proportional to the absorption cross-sections is made.

![Graph showing integrated LIF signals versus excitation wavelength for a $\phi=1.1$, 20bar, CH$_4$/O$_2$/Ar flame using three different bandpass: 320-370nm (square), 280-320nm (round), and Rel. Ex. Wave. (triangle) which is a bandpass from +10 to +60nm red-shifted of the excitation wavelength. The temperatures in the legend are determined from a simple linear regression of the logarithmic plot of the LIF intensity using CO$_2$ absorption cross-sections.](image)

**Figure 5-7** Integrated LIF signals versus excitation wavelength for a $\phi=1.1$, 20bar, CH$_4$/O$_2$/Ar flame using three different bandpass: 320-370nm (square), 280-320nm (round), and Rel. Ex. Wave. (triangle) which is a bandpass from +10 to +60nm red-shifted of the excitation wavelength. The temperatures in the legend are determined from a simple linear regression of the logarithmic plot of the LIF intensity using CO$_2$ absorption cross-sections.

The wavelength-dependence of the absorption cross-section yields estimates for the temperature based on the data in ref [109]. The inferred temperature is around 4000 K, indicating that the decrease of signal with excitation wavelength is not as strong as would be expected from the CO$_2$ absorption coefficient. Furthermore, it shows that the assumption of wavelength-independent fluorescence quantum yield is not valid. For quantitative measurements of CO$_2$ concentrations via LIF, both temperature and wavelength dependence of the fluorescence yield will be required through additional experiments. For the purposes of this study, a qualitative comparison as presented above is sufficient.
Figure 5-8 Adiabatic flame temperatures (triangles), calculated CO$_2$ number densities (squares) and resulting CO$_2$ absorbance (round) number densities for various equivalence ratio in a $\phi=0.9$, 20bar CH$_4$/O$_2$/Ar flame.

Figure 5-9 The LIF intensity plotted as a function of equivalence ratio. Detection wavelength range of 320–370nm is used for the signal integration.
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The dependence of CO$_2$-LIF intensity on the absorbance was also investigated. CO$_2$ absorbance is determined by multiplying CO$_2$ number density with the CO$_2$ absorption cross-sections (Schulz et al.,[109]). For calculation of both number density and absorption cross-sections, local flame temperature is required. For the current study, adiabatic flame temperatures (calculated using ‘chemical equilibrium assumptions’) were used as a function of the equivalence ratio [120]. Calculations of CO$_2$ number density, CO$_2$ absorbance and adiabatic temperatures are plotted in Figure 5-8 as a function of equivalence ratios for a 20bar CH$_4$/O$_2$/Ar flame.

![Figure 5-10 CO$_2$-LIF intensity (320–370nm bandpass) versus CO$_2$ absorbance (calculated from CO$_2$ number density and temperature-dependent absorption cross-section) for 235.88nm excitation. The symbols represent measurements at different equivalence ratios $\phi$; the linear fit represents the case of invariant fluorescence quantum yield for all conditions.](image)

The fluorescence intensity is measured from the spectrally resolved 1-D line-imaging data and is shown in Figure 5-9 as a function of equivalence ratio for a 20bar CH$_4$/O$_2$/Ar flame with a detection wavelength range of 320–370nm. Signal intensities for $\phi$>1.5 shows strong influence from the PAH emission. With the 0$^{th}$-order assumption that the
CO₂ fluorescence yield is independent of temperature and gas composition, the measured fluorescence should be directly proportional to CO₂ absorbance. Figure 5-10 shows that the CO₂-LIF intensity correlates well with the CO₂ absorbance. While these results are sufficient for the purpose of providing qualitative identification of the broadband emission, accurate temperature measurements are required to allow a more accurate confirmation of CO₂ as well as provide the relative dependence of the CO₂ fluorescence quantum yield on temperature variation.

5.3.3 CO₂ UV Spectroscopy

The exact mechanisms for CO₂ UV LIF have yet to be clearly defined and are a topic for further research. Here, an interpretation of the CO₂ LIF spectroscopy is presented, based on currently available literature on CO₂ spectroscopy.

![Energy Diagram for the CO(1Σg⁺, 0(6,7)) = CO₂ System](image)

**Figure 5-11** Potential energy curves for CO₂ taken from ref. [121]. Intersystem crossing occurs between the \(^{1,3}B_2\) states.
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CO₂ electronic structure

The electronic ground state of CO₂ is a \( ^1\Sigma^+ \) state with linear (point group \( D_{\infty h} \)) symmetry \[122\]. The highest occupied molecular orbital (HOMO) is a degenerate \( \pi_g \) orbital, followed by a \( \sigma_u \) orbital; the lowest unoccupied molecular orbital (LUMO) is a degenerate \( \pi_u^* \) orbital. The lowest-energy MO excitation is expected to be \( 1\pi_g \rightarrow 2\pi_u \), which gives rise to \( ^1,^3\Sigma_u^- \), \( ^1,^3\Delta_u \), and \( ^1,^3\Sigma_u^+ \) excited states. The other low-energy MO excitation is \( 3\sigma_u \rightarrow 2\pi_u \), yielding \( ^1,^3\Pi_g \) excited states, depending on the electron spins and the partitioning in the molecular orbital. Calculations have shown that the lowest excited electronic states of CO₂ are \( ^3\Sigma_2^+, ^3\Sigma_2^-, ^3\Pi_0, ^1\Pi_0 \), which all have bent symmetry (point group \( C_{2v} \)) \[123\]. For the bent \( ^1,^3\Sigma_2^+ \) states, the energy versus the OC-O distance is plotted qualitatively in Figure 5-11. Note that the singlet and triplet potential surfaces cross and inter-system-crossing (ISC) caused by a spin change can take place.

State energies from CO₂ absorption data

Recent CO₂ absorption cross section measurements using shock-heated CO₂ \[109\] show that for fixed wavelength, the absorption cross section (\( \sigma \)) increases with temperature. The Arrhenius plots of \(( \ln \sigma ) \) versus \( (1/T) \) over the relevant temperature range (~800–2500K) typically exhibits a linear behavior. From the slope of the linear fits, the ground state energy of involved in the excitation can be estimated. This can be interpreted as excitation of the bending vibrational mode necessary to yield finite Franck-Condon overlap factors with the bent excited states of CO₂. An example of the Arrhenius plots of the absorption cross-sections for the different wavelengths used in this study are shown in Figure 5-12.

It can be seen from Figure 5-12 that the plots are perfectly linear for low temperatures with slight deviation for temperatures over 1700K \((1/T<0.0006)\). This effect is more pronounced for higher wavelengths. The deviation from linearity may be an effect caused by the empirical fits used to determine the absorption cross-sections from ref. [110]. For determination of the ground state energy, each plot is re-fit linearly between 900 and 2500K.
**Figure 5-12** Arrhenius plots of absorption cross-section as a function of temperature for different excitation wavelengths used in this study.

<table>
<thead>
<tr>
<th>Excitation Wavelength (nm)</th>
<th>Photon Energy (eV)</th>
<th>Ground State Energy (eV)</th>
<th>Excited State Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>215.7</td>
<td>5.74838</td>
<td>0.61594</td>
<td>6.36432</td>
</tr>
<tr>
<td>220.9</td>
<td>5.61306</td>
<td>0.65845</td>
<td>6.27151</td>
</tr>
<tr>
<td>226.1</td>
<td>5.48397</td>
<td>0.70102</td>
<td>6.18499</td>
</tr>
<tr>
<td>233.7</td>
<td>5.30563</td>
<td>0.76322</td>
<td>6.06885</td>
</tr>
<tr>
<td>235.9</td>
<td>5.25615</td>
<td>0.78124</td>
<td>6.03739</td>
</tr>
<tr>
<td>242.1</td>
<td>5.12154</td>
<td>0.83198</td>
<td>5.95352</td>
</tr>
<tr>
<td>248</td>
<td>4.9997</td>
<td>0.88031</td>
<td>5.88002</td>
</tr>
<tr>
<td>251.7</td>
<td>4.9262</td>
<td>0.9106</td>
<td>5.83681</td>
</tr>
<tr>
<td>255.9</td>
<td>4.84535</td>
<td>0.94494</td>
<td>5.79029</td>
</tr>
</tbody>
</table>

**Table 5-1** Analysis of the ground state and excited state energies for the excitation wavelengths used in this study.
Chapter 5

The slope yields the minimum ground state energy of CO₂ molecules in order to be absorbed, and from this and the photon energy (wavelength of excitation), the respective excited state level energy can be calculated. The results are given in table 5-12.

Table 5-1 shows that higher ground state levels of CO₂ are excited with increasing excitation wavelength. However, due to the decrease of the photon energy, the energy of the final excited states is decreased. It can be concluded from Table 5-1 that UV light absorption in the 200–300nm range leads to population of the bent ʻB₂ state, in which the lowest energy level is 5.74 eV above ground state energy. This is consistent with the observation of red-shifted emission maximum at higher wavelengths. The same excited state is also populated by the CO(ʻΣ⁺) + O(ʻP) recombination reaction which produces the so-called CO flame bands, which is addressed in the following subsection.

CO₂ LIF Mechanism

A set of the most relevant reactions involved in CO₂ LIF are presented in this section. The discussions are based on available literature on absorption, photodissociation and luminescence of CO₂ [109, 110, 121-131], which provides a relatively consistent interpretation of CO₂ spectroscopy. The most relevant reactions for consideration are shown in table 5-2, and discussed in more detail below.

<table>
<thead>
<tr>
<th>number</th>
<th>Reaction</th>
<th>Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>CO₂ (ʻΣ⁺) + hν → CO₂ (ʻB₂)</td>
<td>Ab</td>
<td>absorption into ʻB₂</td>
</tr>
<tr>
<td>(2)</td>
<td>CO₂ (ʻB₂) → CO₂ (ʻΣ⁺) + hν</td>
<td>A</td>
<td>fluorescence from ʻB₂</td>
</tr>
<tr>
<td>(3)</td>
<td>CO₂ (ʻB₂) → CO₂ (ʻΣ⁺)</td>
<td>ISC</td>
<td>Spin change</td>
</tr>
<tr>
<td>(4)</td>
<td>CO₂ (ʻB₂) + M → CO₂ (ʻΣ⁺)</td>
<td>Q¹</td>
<td>quenching of ʻB₂</td>
</tr>
<tr>
<td>(5)</td>
<td>CO₂ (ʻΣ⁺) + M → CO₂ (ʻΣ⁺)</td>
<td>Q³</td>
<td>quenching of ʻΣ⁺</td>
</tr>
<tr>
<td>(6)</td>
<td>CO₂ (ʻΣ⁺) + O(ʻP) + CO (ʻΣ⁺)</td>
<td>D</td>
<td>Dissociation out of ʻΣ⁺</td>
</tr>
</tbody>
</table>

Table 5-2 Key reactions involved in the CO₂-LIF mechanism.
High Pressure CO₂ UV LIF

- **Reaction (1):** In the previous section, it was shown that absorption occurs out of vibrationally excited modes of the ground state into the bent \( ^1B_2 \) states. State energies of CO₂ indicate that for excitation wavelengths relevant to this study (210–260nm), CO₂ is being populated into levels of the \(^1B_2 \) state with a total energy of ca. 5.8-6.4 eV. There may be also some absorption into the \(^1A_2 \) state; however this is expected to be much weaker and of negligible impact in the LIF process.

- **Reaction (2):** Broadband radiation out of the \(^1B_2 \) state has been documented for CO₂ as far back as the 1930. The faint continuous spectra of CO+O₂ flames (“CO flame bands”, 250–800nm) have been attributed to this radiative process. Similar emission is also observed from O+CO reactions in discharge tubes (after dissociation of CO₂ or by reaction of CO from independently produced O atoms), in shock tubes (after dissociation of CO₂), and also in flames other than CO+O₂. The fluorescence rate calculated from kinetic data is projected to be around \( A=2-6\times10^6/s \). The blue-shift of the CO₂ LIF emission in comparison to the flame luminescence is still unclear. Excitation for CO₂ mainly occurs into levels 5.8–6.2eV above the ground state and O+CO molecules at 2600K (adiabatic temperature) have a total internal energy of \(~6.48\)eV above the CO₂ ground state. However, excited CO₂ formed from O+CO may require ISC \((^1B_2 \rightarrow ^3B_2)\) at a lower energy threshold than the direct UV excitation used in this study. In addition, third body reactions involved in O+CO combination may also contribute to fluorescence of less energy. Further study of excited upper levels of CO₂ leading to LIF emission is required.

- **Reaction (3):** Singlet-triplet crossing is very effective (ISC > 10⁹/s) across the \(^1B_2 \) and \(^3B_2 \) potential surfaces. The fast spin crossing mechanism is proposed as an explanation for the experimental observation of linear laser energy dependence (single-photon absorption; no saturation because of fast ISC), linear pressure dependence (fluorescence lifetime is not quenching limited due to fast ISC) and fast fluorescence decay time (5ns upper limit). It also should be noted that the surface crossing point probably is close to the \(^1B_2 \) ground state energy (which is 5.74 eV above the electronic ground state).

- **Reactions (4),(5) and (6):** Very little is known about CO₂ quenching. Quenching of the \(^1B_2 \) state is assumed to be slower than spin crossing \((^1B_2 \rightarrow ^3B_2)\) since the quantified
Chapter 5

LIF from this study show that the fluorescence yield is constant for pressures up to 40 bar ($\phi = A / (ISC + A + Q^i) \approx \text{const}$). Fluorescence yield in this case is limited by the fast ISC and not by quenching. Dissociation (6) is only possible after spin crossing (direct dissociation to O ($^1\text{D}$) requires 7.41 eV, while dissociation to O ($^3\text{P}$) only 5.45 eV). Due to the fast ISC, most of the initial population is expected to arrive in the $^3\text{B}_2$ state. Since photodissocation yields are typically 10−20% in the wavelength range of 226−230nm, $Q^3$ is expected to be a few times larger (4−9) than the dissociation rate in our experimental conditions.

![Spectrally dispersed emission](image)

**Figure 5-13** Spectrally dispersed emission in $\phi=0.83$, 60bar, CH$_4$/air flame with excitation in the NO $A-X (0,2)$ O$_{12}$-bandhead (247.94nm).

5.3.4 CO$_2$ LIF as Interference in NO-LIF

The broadband emission features of CO$_2$ LIF overlap with both the $\gamma$ bands of NO and the Schumann-Runge bands of O$_2$. Therefore, CO$_2$ can be a significant interference source in the detection of both species. For this study, CO$_2$ interference is most pronounced when using red-shifted detection with $A-X(0,2)$ excitation when the NO signal is relatively low compared to that of CO$_2$. Figure 5-13 shows an emission
spectrum in a $\phi=0.83$ CH$_4$/air flame at 60bar with NO $A-X(0,2)$ O$_{12}$-bandhead excitation at 247.94nm. The flame is doped with 300ppm of NO. The NO and O$_2$ fluorescence lines are superimposed on a significant broadband emission of CO$_2$-fluorescence. It can be clearly seen that for these conditions, CO$_2$ becomes the dominant source interference for red-shifted detection of the NO signal, regardless of applying filters for isolation of a specific spectral region in the emission.

Table 5-3 Ratio of LIF signals from CO$_2$ and NO for various excitation and detection strategies as a function of pressure in a CH$_4$/air flame with 300ppm of NO. CO$_2$ in the post flame gases can be estimated using equilibrium assumptions.

<table>
<thead>
<tr>
<th>NO $A-X$ Band</th>
<th>(0,0) excitation</th>
<th>(0,1) excitation</th>
<th>(0,1) excitation</th>
<th>(0,2) excitation</th>
<th>(0,2) excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0,1)+(0,2) detection</td>
<td>(0,0) detection</td>
<td>(0,2)+(0,3) detection</td>
<td>(0,0)+(0,1) detection</td>
<td>(0,3)-(0,4) detection</td>
</tr>
<tr>
<td>(0.83) Signal Ratio : CO$_2$-LIF/NO-LIF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1bar</td>
<td>0</td>
<td>0</td>
<td>0.00664</td>
<td>0.03521</td>
<td></td>
</tr>
<tr>
<td>5bar</td>
<td>0</td>
<td>0</td>
<td>0.01832</td>
<td>0.09717</td>
<td></td>
</tr>
<tr>
<td>10bar</td>
<td>0</td>
<td>0.00372</td>
<td>0.00632</td>
<td>0.04564</td>
<td>0.24213</td>
</tr>
<tr>
<td>20bar</td>
<td>0.00324</td>
<td>0.02574</td>
<td>0.04371</td>
<td>0.13998</td>
<td>0.74257</td>
</tr>
<tr>
<td>40bar</td>
<td>0.04192</td>
<td>0.06941</td>
<td>0.11785</td>
<td>0.44194</td>
<td>2.34469</td>
</tr>
<tr>
<td>60bar</td>
<td>0.08949</td>
<td>0.13971</td>
<td>0.23723</td>
<td>0.7664</td>
<td>4.06726</td>
</tr>
<tr>
<td>(0.13) Signal Ratio : CO$_2$-LIF/NO-LIF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1bar</td>
<td>0</td>
<td>0</td>
<td>0.00588</td>
<td>0.03121</td>
<td></td>
</tr>
<tr>
<td>5bar</td>
<td>0</td>
<td>0</td>
<td>0.01496</td>
<td>0.07936</td>
<td></td>
</tr>
<tr>
<td>10bar</td>
<td>0</td>
<td>0.00244</td>
<td>0.00415</td>
<td>0.03373</td>
<td>0.17897</td>
</tr>
<tr>
<td>20bar</td>
<td>0.01278</td>
<td>0.02027</td>
<td>0.03441</td>
<td>0.09825</td>
<td>0.52121</td>
</tr>
<tr>
<td>40bar</td>
<td>0.052</td>
<td>0.05703</td>
<td>0.09683</td>
<td>0.27313</td>
<td>1.44909</td>
</tr>
<tr>
<td>60bar</td>
<td>0.07041</td>
<td>0.08839</td>
<td>0.1501</td>
<td>0.42498</td>
<td>2.2554</td>
</tr>
</tbody>
</table>

The fractions of CO$_2$ LIF for various flame conditions using different excitation-detection strategies were previously presented in chapter 4. Here, the ratio of the CO$_2$ LIF to NO LIF (CO$_2$/NO) is presented in Table 5-3 in order to provide a comparison of the two signal strengths as a function of pressure in a CH$_4$/air flame. Five excitation-detection strategies are compared in the $A-X$ bands of NO. Excitation wavelength of
226.03nm ("DiRosa" Line) is used in the $A-X(0,0)$ band, 235.87nm ("B" Line) in the $A-X(0,1)$ band and 247.94nm ("Schulz" Line) is used in the $A-X(0,2)$ band. For the $A-X(0,1)$ and $A-X(0,2)$ transitions, both blue-shifted and red-shifted detection strategies are shown.

### 5.4 Practical Applications of CO$_2$ LIF

#### 5.4.1 Signal Linearity

For practical considerations, the response of CO$_2$ fluorescence signal on pressure and laser fluence is of interest. The CO$_2$ fluorescence signal is linear with laser pulse energy in the 20–700µJ range that was accessible with our dye-laser system. The CO$_2$-LIF signal also increases linearly with pressure in the 1–40bar range. This is shown in Figure 5-14 for a $\phi=0.95$ CH$_4$/Ar/O$_2$ flame. The slight deviation from linearity shown in the right panel of Figure 5-14 is most likely due to the temperature variation of the burner, which peaks at ~20bar.

![Figure 5-14](image)

**Figure 5-14** Linear response of CO$_2$-LIF on laser fluence (left) and pressure (right). For pressure dependence, two excitation wavelengths (226.065nm and 235.86nm) are plotted.
This indicates that the fluorescence lifetime is not limited by fluorescence quenching in the respective pressure range. As previously mentioned, dissociation and fast intersystem crossing (ISC) of the excited CO$_2$ are the lifetime-determining processes proposed as an explanation for this behavior. This is a further reason why CO$_2$ becomes an important interference source in high-pressure LIF diagnostics of species that are strongly affected by collisional quenching, such as NO using excitation in the $A-X$ system. LIF interference for a species with a quenching-dominated quantum yield by LIF from another species whose fluorescence lifetime is limited by fast non-collisional processes causes the signal-to-background ratio to deteriorate linearly with pressure.

**5.4.2 CO$_2$ PLIF Imaging in High-Pressure Flames**

UV planar laser-induced fluorescence (PLIF) images of hot carbon dioxide (CO$_2$) are obtained in a laminar flame (CH$_4$/air) at pressures ranging from 10–60bar with excitation wavelength at 242.14nm. Excitation wavelengths are chosen to minimize the contribution of nitric oxide and molecular oxygen LIF signals. The continuum LIF signal from electronically excited CO$_2$ is detected in a broad (280–400nm) emission region. Although LIF (laser-induced fluorescence) imaging strategies exist for several important chemical intermediates, published strategies for PLIF (planar laser-induced fluorescence) of product CO$_2$ are limited to infrared excitation and detection using vibrational transitions [132, 133]. Unfortunately, vibrational transitions have complex energy transfer, thermal emission is strong in the infrared, and modern high speed infrared camera technology is only emerging; thus, an ultraviolet (UV) method to visualize CO$_2$ is desirable. The UV PLIF of hot CO$_2$ has the potential for application to a wide variety of diagnostic needs in high-pressure flames, combustors, and engines.

**PLIF Imaging Setup**

Images were obtained for $\phi = 0.9$ and $\phi = 1.1$ fuel/air equivalence ratios, where the uniform CO$_2$ core region extends 5mm vertically above the flame. Laser light from the dye laser (described previously in Section 5.2) was formed into a vertical light sheet ($10 \times 0.5\text{mm}^2$) crossing the flame horizontally, where it illuminated a cross section through the center of the flame 1–10mm above the burner matrix. The pulse energy was
measured with a photodiode (LaVision) and registered around 2mJ/pulse @ 235–243nm with a 0.25 cm\(^{-1}\) FWHM spectral width. Fluorescence signals were collected at right angles to the laser beam and focused with a \(f=105\)mm, \(f/4.5\) achromatic UV-lens (Nikon) onto the chip of an intensified CCD camera (LaVision Dynamight). The signal light was discriminated against elastically scattered light with a 280nm long-pass dielectric filter (Optosigma), and through an internal transmittance UV-transmitting bandpass filter (120nm bandpass, center @340nm, Optosigma). To quantify the O\(_2\)-LIF contribution in our images, a spectrometer (Chromex 250IS) was used with the camera for spectrally resolved detection of line images of CO\(_2\) and O\(_2\) LIF.

**Figure 5-15** Simulated LIF excitation spectra of O\(_2\) (upper) and NO (lower) at 20bar and 2000K (LIFSim [10]). A magnified O\(_2\) spectrum near the excitation wavelengths is also shown. 239.34nm and 242.14nm excitation lines are shown with arrows.

**Selection of Excitation and Detection Wavelength**
Detection of CO₂ in high-pressure flames is complicated by the following issues. Excitation of CO₂ in the 200–300 nm spectral region directly overlaps with excitation of the $A^2Σ^+−X^2Π$ γ bands of NO and the $B^3Σ^+−X^3Σ^+$ Schumann-Runge bands of O₂ [17]. Pressure broadening increases this overlap. Finding an excitation wavelength where both species are minimized is difficult due to the widely pervasive nature of O₂ bands in this region. The strategy is to use excitation wavelengths which avoid overlap with NO transitions in the region, while at the same time, minimizing the overlap with the multiple vibrational bands of O₂. Based on spectral simulation models (LIFSim [10]) and experimental excitation scans, two candidate excitation wavelengths (239.34nm and 242.14nm) show the best level of performance. The two transitions, both of which are located between the $A−X(0,1)$ and $A−X(0,2)$ bands of NO, and are shown in Figure 5-15 (lower plot).

In comparison, excitation at 242.14nm was found to provide the least interference from O₂ with sufficient NO minimization, while 239.34nm excitation is more selective in completely avoiding any NO transition. The imaging demonstrations presented in this section were achieved by using excitation at both 239.34nm and 242.14nm with no seeded NO in the flame. The detection window of the CO₂-LIF signal extends from 280 to 400nm. This ensures suppression of Rayleigh scattering as well as Raman scattering from other combustion products. The 400nm upper limit also suppresses background from flame emission, scattered pump-laser, and/or room light.

**CO₂ PLIF Imaging**

CO₂ visualization using UV-LIF in a high-pressure flames (10–60bar) for equivalence ratios of $\phi=0.9$ are shown in Figure 5-16. The resulting images are corrected for laser sheet inhomogeneities and the signal attenuation along the path of the laser beam caused by hot CO₂ and H₂O absorption. Correction of attenuation utilizes recently quantified absorption cross-section data [109, 110] of hot CO₂ as well as flame temperatures obtained from multi-line fitting of NO-LIF excitation scans [116] (discussed in more detail in chapter 6). Attenuation levels for corrections can exceed 10% across the flame length of 8mm in a 20bar flame with excitation at 239.34nm. The LIF signal is also corrected for temperature dependence of the laser excited ground state populations and
fluorescence quantum yield. While the main temperature dependence resulting from variations in the absorption cross section are well-known [109], the fluorescence quantum yield dependence can only be estimated using the variation of LIF intensity as a function of equivalence ratio (hence, temperature), separately obtained from 1-D line-imaging measurements. This correction can only be carried out over a limited temperature range and extrapolated to a wider temperature region. The fluorescence yield corrections are crude at best, and further complicated by the Rayleigh-Taylor instability which causes the outer region, where temperature gradient is large, to flicker. Therefore, the images presented here are semi-quantitative: calibrated at the post flame region (2.5mm above burner) using number density calculations from thermal equilibrium calculations [120].

**Figure 5-16** CO₂ PLIF images of φ=0.9 CH₄/air flames for pressure range of 10 to 60bar. Two excitation wavelengths (239.34nm and 242.14nm) are shown.

It can be observed that CO₂-LIF intensities remain fairly constant to a first-order estimate throughout the hot burnt gas region. It should be noted that the images are also influenced by slight O₂ interference. Excitation wavelength of both 239.23nm and 242.14nm, while chosen to minimize contribution from O₂-LIF, cannot fully suppress the
signal. The outer regions of the hot gas are more pronounced due to the entrainment of O\textsubscript{2} from the coflow air. This effect is more evident with 242.14nm, where O\textsubscript{2} suppression is less effective. Overall, the impact of O\textsubscript{2} interference is small and accounts for less than 7\% in the most O\textsubscript{2} dominant condition (φ=0.9, 60bar) in the center region of the post combustion gases. For the dye laser setup used in these experiments, both wavelengths are well situated near the maximum power band of the Coumarin 102 laser dye, and power was readily available.

5.5 Conclusion

Broadband laser-induced fluorescence following excitation in the 215–255nm range was investigated in various flames at elevated pressures and attributed to CO\textsubscript{2}. The CO\textsubscript{2}-LIF signal consists of a broad (200–450nm) continuum with a faint superimposed structure. Signal variations with excitation wavelength, equivalence ratio and flame temperature correlated well with CO\textsubscript{2} absorption cross-sections. The signal is also clearly distinguishable from LIF emission of polycyclic aromatic hydrocarbons found in very rich combustion conditions. The broadband CO\textsubscript{2} signal completely disappears in carbon-free flames. While the temperature dependence of LIF intensities shows only minor deviations from the correlation with absorption cross sections, a systematic variation of the fluorescence quantum yield was shown with different excitation wavelengths.

The CO\textsubscript{2} LIF increases linearly with pressure, making CO\textsubscript{2} a potential source of interference in high-pressure detection of collisionally quenched species. In turn, CO\textsubscript{2} fluorescence might open up new opportunities for diagnostics for isothermal high-pressure mixing processes or for temperature in high-pressure systems with constant CO\textsubscript{2} concentration. As a demonstration for visualization of CO\textsubscript{2} using UV LIF, semi-quantitative PLIF images of hot CO\textsubscript{2} using UV excitation in the burnt gases of premixed, high-pressure laminar flames were presented. Excitation wavelength of CO\textsubscript{2} was optimized for suppression of interference from both the γ bands of NO and the Shumann-Runge bands of O\textsubscript{2}. Further study regarding the temperature dependence of CO\textsubscript{2}
Chapter 5

fluorescence quantum yield is required for a more accurate and quantitative analysis of CO$_2$-LIF.
Chapter 6 Quantitative Multi-Line NO-LIF Thermometry

In this chapter, an accurate temperature measurement technique for steady, high-pressure flames using excitation wavelength-scanned laser-induced fluorescence (LIF) within the nitric NO $A-X(0,0)$ band is presented. Multi-line thermometry can be used for single point, line or 2-D imaging of temperature. Measurements are made in premixed methane/air flames at pressures between 1 and 60bar with a fuel/air equivalence ratio of 0.9. Excitation spectra are simulated with a computational spectral simulation program (LIFSim) and fit to the experimental data to extract gas temperatures. The LIF scan range was chosen to provide sensitivity over a wide temperature range and minimize LIF interference from oxygen. In addition, fluorescence emission spectra were also analyzed to quantify the contribution of background signal (mainly CO$_2$) and investigate interference in the detection bandwidth. The NO-LIF temperatures are in good agreement with intrusive single-color infrared pyrometry measurements additionally made in the high-pressure burner. Multi-line thermometry can potentially be a useful tool to study high-pressure flame chemistry as well as provide a standard to evaluate and validate fast-imaging thermometry techniques for practical diagnostics of high-pressure combustion systems.

6.1 Background

6.1.1 Temperature Measurements via Laser Spectroscopy

Temperature is one of the key quantities in combustion. It governs reaction chemistry (reaction rates and equilibrium states) and pollutant formation processes. In practical systems, accurate and precise determination of temperature enables optimization of combustor efficiency, as well as minimization of pollutant emissions. Temperature in flames and non-reacting flows can be determined by probe techniques
Chapter 6

[3], but these potentially perturb the reactive flow and affect reaction chemistry. Other
diagnostic methods include laser-based non-intrusive spectroscopic techniques [1, 134]
as reviewed by Stricker [135] and Laurendeau [29]. Spectroscopic methods either rely on
the population dependence of different rotational, vibrational, or electronic states of the
target atom/molecule (spontaneous Raman scattering, LIF, coherent anti-Stokes Raman
scattering (CARS), absorption spectroscopy) or exploit the change of density utilizing
ideal gas arguments to obtain temperatures (Rayleigh scattering, spontaneous Raman
scattering). Coherent anti-Stokes Raman scattering (CARS) [136, 137] typically provides
the highest accuracy, but is experimentally complex and produces only single point
measurements. Laser absorption methods [138] are generally limited to line-of-sight
integrated measurements. Rayleigh scattering [139, 140] is relatively simple to
implement, but requires knowing the local gas composition (i.e. the effective scattering
cross section). In addition, unfiltered Rayleigh scattering suffers from elastic scattering
off surfaces and Mie scattering by particles. Spontaneous Raman scattering [141] is
robust against scattering effects, but signals are weak and spectrally-resolved detection is
often required for accurate analysis, in which case 2-D imaging becomes difficult. Laser-
induced fluorescence (LIF) [33] can potentially yield spatially-resolved images of the
selected target species, but often requires detailed spectroscopic parameters such as
fluorescence yield, quenching, energy transfer, etc. for precise measurements.

Practical applications of temperature measurements using LIF in the literature are
discussed in more detail in the next section. While these spectroscopic techniques have
been widely applied in combustion research, an accurate fast-imaging temperature
measurement technique for practical high-temperature and high-pressure combustion
systems is still an elusive target and a topic for further investigation. The motivation for
this study is to provide a validation tool for development of such fast-imaging techniques
and for detailed study of high-pressure flame chemistry by enabling accurate and
spatially resolved temperature measurements in steady systems. Note that this method is
not suited for applications in practical devices where fluctuating combustion conditions
require fast detection for freezing the flow structure.
6.1.2 Applications of LIF Thermometry

Laser Induced Fluorescence (LIF) is suitable for temperature imaging due to its species selectivity and strong non-resonant signals. LIF can selectively probe different rotational, vibrational or electronic states, where the relative equilibrium population depends on the temperature as given by a Boltzmann distribution [19]. The choice of the target molecule for LIF thermometry influences the accessible temperature range, versatility of the technique, experimental approach, and spectroscopic evaluation procedure. Temperature measurements have been performed using atomic fluorescence tracers like indium [142-144], diatomic tracers like OH [145-152], NO [7, 31, 33, 45, 149, 151-161], O₂ [146, 162-165], iodine [166, 167], CH [158] and C₂ [158], and fuel-tracers like ketones [168-170]. The availability of these molecules differs in reactive systems. The presence of OH and hot O₂ is limited to regions after the flame front in combustion processes; the indium technique requires the activation of a precursor within the flame front; CH and C₂ are short-lived combustion intermediates present in close vicinity of the flame front only; fuel tracers are only available in unburned gases and are therefore limited to temperature imaging of unburned mixtures. Nitric oxide (NO), seeded to reactive flow systems, has the advantage of being present in both, the unburned and the post-flame gases. It is stable in both room temperatures and elevated flame temperatures, enabling measurements of temperature to be made over a wide range.

The basic concept of this study involves fitting excitation spectra obtained from laser-induced fluorescence (LIF) of nitric oxide with simulation data to obtain temperatures. The technique was recently evaluated by Bessler et al. [171] for atmospheric-pressure flames, and the subsequent applications in spray flames and sooting flames up to 5bar have also been demonstrated [172,173]. In particular, atmospheric-pressure flame measurements were compared with CARS measurements for an evaluation of its accuracy [171]. Unfortunately, the approach used at these lower pressures requires adjustments for high-pressure flame conditions (p≤60bar). The main objective of the current work is to extend multi-line NO-LIF thermometry to high-pressure applications; to identify the main problems caused by the elevated pressure and provide a new protocol for data collection. The LIF temperatures in this study are compared with temperatures inferred from an intrusive single-color pyrometer.
measurement of a metal bead probe. In addition, the potential of this thermometry technique for spatially resolved measurements for both 1-D or 2-D imaging of temperature is demonstrated.

### 6.2 Experiment

Demonstrations of multi-line thermometry were carried out in laminar, premixed methane/air flat-flames at pressures from 1–60bar in the Stanford high-pressure burner (Section 3.1.1).

![Experimental setup](image)

**Figure 6-1** Experimental setup for NO-LIF multi-line thermometry (a), and also for an intrusive probe (Pt/Rh bead) infrared pyrometer measurement (b).

Investigations were conducted for a $\phi=0.9$ fuel/air equivalence ratio. Laser pulse energy was $1\pm0.2\text{mJ/pulse}$ (7ns pulse at 10Hz) from a Nd:YAG-pumped (Quanta Ray GCR250) frequency-doubled (BBO) dye laser (LAS, LDL205). The beam was weakly focused ($0.5x0.5\text{mm}^2$) along a line 3mm above the burner matrix and crosses the flame horizontally (Figure 6-1 (a)). The pulse energy was monitored with a fast photodiode
Quantitative Multi-Line NO-LIF Thermometry

1-D line-imaging was used where fluorescence signals were collected at right angles to the laser beam and focused with a $f=105\text{mm}$, $f/4.5$ achromatic UV-lens (Nikon), dispersed spectrally through an imaging spectrometer (LaVision Chromex 250IS) and imaged onto the chip of an intensified CCD camera (LaVision Dynamight). The resulting two-dimensional image yields spatial resolution along one axis (8mm) and emission wavelength (230–310nm) on the other. Elastically scattered laser light was suppressed by using a reflective dielectric filter (HR, FWHM 10nm, centered around 226nm, Laser Optik).

For the probe/pyrometer measurements, a platinum/rhodium (Pt/Rh) bead (0.5mm diameter, Oriel type R bead) was suspended 4mm above the flat flame in the post flame gas region (Figure 6-1 (b)). Detection was via a single-color infrared pyrometer with a measurement range of 600–3000°C (Minolta-Land Cyclopes Model 152 Infrared Optical Pyrometer). The bead provided sufficient detection area for uniform emissivity in the lock-in zone (as seen through the viewfinder) of the pyrometer, and calibration of emissivity to black body radiation was carried out at 1bar using standard thermocouple measurements. The pyrometer measurements were also corrected for radiation losses, which will be discussed in more detail in Section 6.4.3. Heat transfer analysis also shows that conduction losses from the bead to the base of the matrix via the suspension wire and subsequent convection from relatively cold coflow can account for a temperature difference of less than 15K.

6.3 Multi-Line NO-LIF Thermometry

6.3.1 Basics of Multi-Line NO-LIF Thermometry

The multi-line NO-LIF thermometry presented here is based on an excitation scan of laser wavelength over a number of lines in the rotational manifold of the NO $A-X(0,0)$ transition; this spectrum is then fit using a numerical spectral simulation to extract temperature. Multi-line thermometry has also proven to be robust against elastic scattering from surface or particles, as well as against broadband LIF from polycyclic aromatic hydrocarbons (PAHs) and CO$_2$ [114] or laser-induced incandescence (LII).
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[113] from soot. While NO-LIF multi-excitation strategies have been previously applied to low-pressure flames [152], atmospheric-pressure flames [151, 157] and in an arc-jet reactor [158], the first use of entire NO-LIF excitation spectra (NO $A-X(0,0)$ band) for temperature measurements in high-pressure flames was by Vyrodov et al. [7] in 1995, where accurate thermometry was demonstrated in flames up to 20bar.

The purpose of this study is to extend the NO LIF multi-line thermometry strategy of Bessler and Schulz [171] to high pressures ($p \leq 60$bar). The NO excitation spectrum is calculated for given fit temperature using LIFSim [10] to account for the collisional broadening and interference from oxygen. Specific issues for discussion in this chapter involve problems caused by the elevated pressure (i.e. interference issues, signal attenuation, NO reburn etc.), implementation of statistical sensitivity analysis for optimizing data acquisition parameters, analysis of new data acquired with the new protocol and the implementation of a more flexible computational fitting routine to allow flexible control over individual fitting parameters. Most importantly, the accuracy and applicable pressure range of this multi-line thermometry technique is quantitatively assessed. An important practical problem is the careful determination of the LIF signal in the absence of NO (or the baseline), and this is discussed here in detail. Because the data acquisition requires a wavelength scan, the technique as presented is only applicable to steady combustion and flow systems or to repetitive systems where phase-locked sampling is possible.

LIFSim [10] is used for computational modeling of the NO and $O_2$ spectroscopy and implements a full spectroscopic database of NO $A-X$ term energies and oscillator strengths and including pressure broadening and collisional quenching. LIFSim is based on a non-transient three-level model of NO (1: ground level, 2: excited level, 3: rotational manifold in ground level). Fast rotational energy transfer (RET) is assumed between levels 1 and 3, which leads to continuous thermal equilibrium, where a Boltzmann distribution is assumed for the ground-state population. Additional RET and vibrational energy transfer (VET) processes [27] are not considered in the version used in the current study.
6.3.2 Choice of Excitation Scan Range

The LIF excitation scan range used in this study extends from 225.944nm to 226.112nm (Figure 6-2). It is a compromise between temperature sensitivity, applicable excitation scan range, data acquisition time and suppression of interference signal from other species. The spectral region covers 41 NO rotational transitions which are blended into 14 distinct features at atmospheric pressure. This scan region is sensitive over a wide range of ground state energies extending from room temperature to 3500K. At higher pressures, the spectrum is significantly altered by collisional broadening (overlap of rotational lines) and shifting [20-22] as demonstrated by the NO excitation spectrum at 20bar in Figure 6-2. This produces a general reduction in intensity leading to a reduced signal-to-noise (SNR) ratio. Therefore, it is important to implement a computational model which can accurately account for these phenomena.

![Figure 6-2](image.png)

**Figure 6-2** Numerical simulation (LIFSim) of NO and O2 LIF-excitation spectra in the range of 225.8nm–226.2nm at 2000K. Scan range (225.944–226.112nm) is located in region of minimum O2-LIF interference.
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NO \( A^1\text{X} \) transitions in high-pressure combustion gases also suffer from interference by other species, most notably LIF from multiple vibrational bands of \( \text{O}_2 \) [17] and broadband \( \text{CO}_2 \) LIF (280–400nm) [114]. Simulated \( \text{O}_2 \)-LIF excitation spectra are also shown in Figure 6-2. The specific scan region in this study has previously been identified by DiRosa et al. [8] as having minimal interference from the \( B^1\text{X} \) Schumann-Runge bands of \( \text{O}_2 \) [17]. It can be seen that the entire scan region is void of any strong \( \text{O}_2 \) transitions.

![Simulated O2-LIF excitation spectra](image)

**Figure 6-3** Example of sensitivity analysis using simulated spectra with added noise (Gaussian) and fitted to extract temperature at 20bar. (225.944–226.112nm region) Random Gaussian noise is added to the simulated spectra for temperature fitting to simulate experimental conditions.

The choice of optimal scan range and data collection strategy is an important issue since applicable temperature range and temperature precision is influenced by these factors. To optimize temperature sensitivity, we extend the 1bar analysis of Bessler and Schulz [171] and adapt a statistical analysis based on multi-line fitting of simulated spectra with synthetic Gaussian noise as shown in Figure 6-3. The synthetic noise characteristics are chosen to reflect the noise characteristics of our detection system.
Figure 6-4 Sensitivity analysis of temperature fitting with respect to scan wavelength range for 2000K. The scan range centers around 226.03nm (O₂-LIF suppression region). Signal from 40 laser pulses is averaged on chip for each individual data point.

Figure 6-5 Sensitivity analysis of temperature fitting with respect to the number of individual laser experiments that are averaged on chip at each wavelength position for 2000K. Scan range is 225.944–226.112nm.
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The procedure is repeated 200 times and the standard deviation of the 200 fitted temperatures becomes a measure for the precision of the fitting technique. For a variety of starting wavelengths, pressures, scan ranges and number of laser pulses averaged, the condition which provides minimal standard deviation is then identified as being the optimal scan range. For the precision and accuracy of the multi-line thermometry method in this study, sensitivity analysis indicates that a local minimum in standard deviation of temperature exists around 226.03nm where interference from $\text{O}_2$ is minimized (a global minimum exists around a scan origin of 225.22−225.47nm, but is influenced by $\text{O}_2$-LIF).

Additional simulations were carried out to assess the scan region length (Figure 6-4) and the effect of varying the number of laser shots whose signal is averaged during data collection (Figure 6-5) for different pressures. While it is obvious that longer scan regions will result in higher precision, Figure 6-4 illustrates the relative increase in sensitivity with increased scan region. This information is used to determine the length of scan region for a target sensitivity. In the same way, Figure 6-5 is used to determine the influence of on-chip averaging on temperature sensitivity. Both of these results indicate a loss of sensitivity with increasing pressure due to declining SNR ratio. Target precision for the current thermometry was a subjective 5% (±100K at 2000K, horizontal bar in Figure 6-4 and Figure 6-5). While additional uncertainties in the experimental setup reduce the precision and accuracy in the results even further, statistical sensitivity analysis provides a theoretical limit of performance, along with a guideline for use in the actual experiments.

6.3.3 Data Evaluation

The multi-line NO-LIF thermometry technique, has the potential for imaging measurements with a detection bandpass selected with filters in front of the camera [171] and a demonstration is shown in Chapter 6.5. In this section, spectrally resolved measurements are obtained with one-dimensional spatial resolution along the laser line over the range of 230−310nm. This arrangement allows the monitoring of the quality of NO LIF, and to assess the interference and background signals by other species. It also allows flexible control of the detection bandpass for future data evaluation. For each
Quantitative Multi-Line NO-LIF Thermometry

point in the excitation scan, the camera collects an image with the spatial resolution along the horizontal path of the laser beam on the vertical axis and spectrally-resolved emission spectra on the horizontal axis (Figure 6-6).

Data from multiple laser shots are integrated on the CCD chip of the detection camera and then corrected by the average laser intensity. The laser pulse is absorbed in the hot gases by NO, CO$_2$, H$_2$O and O$_2$ [110], of which the dominant absorption is by CO$_2$. At the highest pressures, 40% of the laser light is absorbed in the 8mm path across the burnt gases with an excitation wavelength of 226nm. It is estimated that this laser energy perturbs the flame temperature by less than 20K for the 1mJ/pulse (10Hz) used. The absorption of the subsequent LIF signal is at most 20% for the fluorescence of NO $A-X(0,0)$ and less for the red-shifted detection band used.

Figure 6-6 Raw image from camera at individual point of excitation scan ($p=20$bar, $\lambda_{ex}=226.034$nm). White box in center shows detection region for reconstruction of laser excitation spectrum (detection region is broadband 230–310nm).

In the current study, the laser is scanned from 225.944–226.112nm in steps of 0.001nm, resulting in 168 individual image sets for each scan. The number of laser shots averaged at each wavelength position was increased from 20 to 80 with increasing pressure (1 to 60bar), to compensate for the reduction of SNR. An excitation spectrum is
then extracted by spatially-averaging a broadband detection region in the center of the imaged line (the box in Figure 6-6 shows the 0.7mm wide section that is spatially averaged in the middle of the flame). For NO LIF, the spectral shape of the emission spectra depends strongly on the rotational level that the NO is excited to [115]. Branching ratio (fluorescence vs. rotational energy transfer (RET) rate and quenching rate) arguments suggest that while significant RET is observed, RET rates within the NO $A (\nu' = 0)$ fail to completely redistribute the population in the initially populated state to neighboring states within the fluorescence lifetime. This means that the excited-state population distribution during emission is not in thermal equilibrium. Broadband detection therefore is preferred since it is insensitive to these non-uniform excited-state population distribution effects. Dependence of temperature accuracy on variation of detection bandpass is an ongoing issue for investigation.

### Figure 6-7

Schematic of multi-line fit routine. Sequence 1 (upper) fits all parameters to determine laser lineshape and line positions. Sequence 2 (lower) extracts temperature with reduced number of fit parameters.
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Numerical calculations of NO excitation spectra are fit to experimental data via a non-linear least-square fitting routine (Levenberg-Marquardt algorithm [84]). Measurements in a 1bar flame are used to reduce the number of free parameters needed to fit the high-pressure data. The laser lineshape (combination of Gaussian and Lorentzian terms) and exact position of the excitation lines are fixed to the values found in the 1 bar fits. The peak position of each excitation line is adjusted using the 1bar data to account for inaccuracies in the spectroscopic database and experimental shortcomings of the laser tuning. The spectroscopic database is updated accordingly. The remaining pressure-dependent simulation parameters are temperature (our target parameter), signal strength (gain) and baseline signal (defined here as all signal in addition to NO-LIF). A schematic of the entire procedure is shown in Figure 6-7. The fit is carried out in two steps, which are noted as sequences 1 and 2, respectively. Sequence 1 (upper) shows fitting of all parameters in a 1bar flame to extract laser lineshape and line positions. Sequence 2 (lower) then fits high-pressure data with a reduced number of fit parameters as well as new line positions determined from the 1bar case.

A critical factor for determination of temperature in the high-pressure flame is the exact assessment of the contribution of the baseline signal strength. An example of a typical emission spectrum with NO $A-X(0,0)$ excitation is shown in Figure 6-8 for 10 and 40bar. Note that the signal caused by elastically-scattered laser light overlaps the observed NO $A-X(0,0)$ LIF signal. The detection region extends from 230nm to 310nm where LIF contribution from other species interferes with that of NO. For the fuel lean flames studied here, the majority of the interference in the high temperature burnt gases is LIF from O$_2$ and CO$_2$. The fluorescence lifetime of the relevant excited states of O$_2$ are limited by predissociation, and therefore the pressure influence on line broadening and fluorescence quantum yield is much smaller than for NO. This leads to an increase of the relative contribution of O$_2$-LIF background with increasing pressure. While the excitation scan range avoids strong transitions of O$_2$, the relative interference from O$_2$ LIF does increase with pressure. In addition, the absorption and subsequent fluorescence from hot CO$_2$ [114] increases with pressure and becomes a major contribution to the baseline at pressures above 20bar. The relative increase of O$_2$ and CO$_2$ interference and subsequent contribution to the baseline can be observed in the 40bar data in Figure 6-8.
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Since collisional broadening of the NO transitions causes overlapping of neighboring lines during excitation (Figure 6-1), there is no “off-resonant” position between excitation features for high-pressure conditions and this complicates evaluation of the baseline. The nascent NO concentration in the flames is required to evaluate this baseline, which is then used as a fixed parameter in the multi-line fitting of the high-pressure data.

Figure 6-8 LIF fluorescence spectrum with NO A−X(0,0) excitation at 10 and 40bar. The spectrum is separated into contributions from different components (NO, CO\textsubscript{2} and O\textsubscript{2}-LIF, Rayleigh scattering). Lower part of each plot is magnified for a clearer view of the spectral separation. Baseline is defined as sum of all signals in the detection region (230nm–310nm) excluding NO-LIF. $\lambda_{ex}=226.034$nm (400ppm NO seeding, $\phi=0.9$).

We determine the nascent NO concentration in the flame using a variable NO seeding method and later compare the nascent NO determined to values from multi parameter fitting of the fluorescence spectra. The LIF is measured at two different excitation wavelengths, which have minimal and maximum NO signal strengths,
respectively, as illustrated in Figure 6-9. These wavelengths are selected relatively close together in the target scan range where the baseline intensity can be assumed to be constant for a given pressure (region of minimal O$_2$ interference [8] and constant CO$_2$ LIF [114]).

**Figure 6-9** NO addition method for the determination of the baseline strength and the nascent NO concentration at $p=30$bar. The plot shows a magnified view of the small box in the inserted graph. The NO addition is varied from 200 to 600ppm and NO-LIF is detected with excitation at two different wavelengths. Excitation A and B refer to two different excitation wavelengths. ($\lambda_A : 226.03$nm, $\lambda_B : 226.042$nm). Data taken at 3mm above the burner matrix.

After measuring the total signal at two different wavelengths at several different NO seeding concentrations, the overall signal is linearly fit as a function of NO seeding for each of the excitation wavelengths. These two linear fits are extrapolated to their intersection yielding the nascent NO concentration and the value of the baseline signal. This method is used to determine the baseline level for each flame as a function of pressure and $\phi$. Determination of the nascent NO concentration (and LIF baseline) by this method assumes the NO reburn mechanism is first order in NO concentration. If this assumption was grossly in error the variation with NO seeding in Figure 6-9 would not be linear. In the stoichiometric and lean flames studied here with less than 100ppm NO
addition, the NO reburn is expected to be linear in NO concentration and less than 10% [68, 174, 175]. It has also been experimentally determined that the temperature in the test flames does not vary (≤5%) for NO additions as large as 1500ppm, thus it is expected that the NO formation is relatively independent of the NO seeding.

![Figure 6-10](image-url) NO addition plots for determination of baseline strength at 10, 20, 50 and 60bar. Two lines in each graph are linear fits to the two different excitation wavelengths. Excitation A and B refer to two different excitation wavelengths (λ_A: 226.03nm, λ_B: 226.042nm). Data taken at 3mm above the burner matrix.

6.4 Results and Discussions

6.4.1 Baseline Determination via NO Addition Method

The baseline determination via the NO addition method (discussed above, c.f. Figure 6-9) is shown in Figure 6-10 for 10, 20, 50 and 60bar flames. NO was excited at 2 different wavelength positions (λ_A: 226.03nm, λ_B: 226.042nm) while the NO concentration was varied from 200 to 600ppm in 100ppm intervals.
Two linear fits to the data converge in the lower, left quadrant and provide the baseline and nascent NO concentrations. As pressure approaches 60bar, the slope of the two lines becomes nearly the same and determination of the convergence point becomes difficult. Subsequently, the extrapolation errors increase. The analysis assumes a constant baseline throughout the entire scan region and careful correction is required to match LIF intensity from the NO addition method with the intensity from a specific excitation wavelength of the laser in the excitation spectra, since the baseline contribution to the total signal (baseline/total signal) is dependent on the excitation wavelength of the laser. Note that strong structured O$_2$ LIF is avoided in this region (Figure 6-2) [17] whereas an increased excitation region would require a variable baseline to account for the excitation-wavelength dependence of O$_2$. The baseline signal strength is inferred from the y-axis (LIF Intensity) and used as a constant during the fit.

**Figure 6-11** Nascent NO concentration vs. pressure in a $\phi$=0.9 CH$_4$/air flame. Concentrations are derived from NO addition method. Data taken at 3mm above the burner matrix.

Figure 6-11 shows nascent NO concentrations calculated from the NO addition strategy as a function of pressure. Due to the high temperatures involved, the main NO
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formation mechanism is expected to be via the thermal NO formation (Zeldovich [176]). While the temperature decreases slightly with increasing pressure, an increase in NO concentration is observed with increasing pressure due to the dependence of the Zeldovich mechanism on gas density ($\sim \sqrt{p}$). In addition a slight increase in the prompt NO formation reactions including that involving the intermediate N$_2$O can be considered, although the third body collision (proportional to pressure) requirements for N$_2$O formation is compensated by a reduction of N$_2$O lifetime due to the high temperatures [177]. A more detailed discussion regarding NO concentrations including results of chemical reaction simulations using PREMIX are presented in the next chapter.

Figure 6-12 Multi-line temperature fitting in 1–60bar, $\phi=0.9$ CH$_4$/air flames. (NO seeding at 400ppm). The LIF-Intensity scales of the 30, 40, 50 and 60bar figures have been magnified for viewing clarity.
6.4.2 Spectral Fitting of Excitation Spectra

The result from the multi-line temperature fitting for the 1bar case and higher pressures (CH₄/air flame at φ=0.9) are shown in Figure 6-12. For the 1bar plot, none of the fitting parameters were fixed in the analysis procedure, yielding a laser Gaussian FWHM of 0.21cm⁻¹ and a Lorentzian FWHM of 0.03cm⁻¹, in good agreement with laser specifications. In addition, the observed spectral positions of the absorption features (overlapping rotational lines) were compared to simulated data and adjustments were made to the spectral line database.

NO seeding was 400ppm, a sufficient number density to provide large NO-LIF signal, but small enough not to perturb flame dynamics or temperature [171]. The experimental reproducibility was confirmed by fitting ten repeating scans (max ΔT=40K). Additionally, 1bar scans were conducted at the start and end of each day to check for drift in laser wavelength and for reproducibility of temperature results. The fitting results for higher pressures in Figure 6-12 illustrate that the simulation is able to reproduce the experimental data very well. As the pressure increases, more laser pulses were averaged to compensate for the decrease of temperature sensitivity illustrated in Figure 6-5, resulting in increasing data collection times (e.g., 6 minutes data acquisition time at 1bar to 25 minutes at 60bar). Typical computational time for the fit was around 35 seconds (3GHz Pentium III-PC), and this time is reduced by the use of a spectral database reduced to cover only the transitions in the scan region.

Figure 6-12 also shows the impact of collisional line broadening on the excitation spectra and deterioration of the SNR. Spectral-overlap also reduces the number of NO peaks with increasing pressure, reducing the sensitivity of temperature to the spectral fit. In addition, baseline contribution is enhanced at high pressures due to increased contribution from hot O₂ and CO₂ LIF. As for the applicable pressure range, we find that the fitting of this NO-LIF excitation region works well until 50bar (though slight discrepancies occur at the edges of the scan range at 50bar). The data at 60bar illustrate that this scan region is inadequate to provide good temperature sensitivity at higher pressures due to its loss of structure. The problem is compounded by low signal levels, possible minor inaccuracies in the assumptions of gas composition, potential
inaccuracies in the spectral model, and difficulties in accurate baseline determination for high-pressure fitting. Unfortunately, increasing the scan range increases the excitation-wavelength dependent contribution from O$_2$-LIF. Investigation of the wavelength-resolved LIF data is underway to evaluate other detection bandpasses which can mitigate the O$_2$ contribution, while maintaining the accuracy and precision of the fit.

6.4.3 Quantitative Temperature Measurements

Resulting temperatures obtained from the multi-line fitting technique and pyrometer measurements are shown in Figure 6-13.

![Figure 6-13](image.png)

**Figure 6-13** Temperature vs. pressure for the two different measurement techniques (multi-line fitting, pyrometer) in a $\phi=0.9$, CH$_4$/air flame. Adiabatic temperatures have been calculated using thermal equilibrium model (STANJAN [120]). Data is taken 3mm above the burner matrix.

Temperatures are in good agreement within the error range to 40bar (e.g., $\pm 72$K at 10bar, $\pm 91$K at 20bar, $\pm 120$K at 40bar, $\pm 180$K at 60bar). The error here is a representation of statistical calculation taken from temperature sensitivity analysis (previously discussed in ‘Multi-line NO-LIF thermometry at high-pressure’ section) and additional uncertainties
projected in our experimental setup/data processing procedures. As mentioned before, the quality of the fit starts to deteriorate at 60bar and yields an under-prediction of temperature in comparison to pyrometer measurements. In addition to general loss of structure in high pressure spectra, O\textsubscript{2} transitions outside of our scan range can blend in due to collisional broadening (though weakened by pre-dissociation) and disrupt our assumption of a uniform baseline. Adiabatic temperatures in Figure 6-13 have been calculated using a thermal equilibrium model, STANJAN [120] (fresh gas temperature prior to combustion is 373K for the burner).

**Radiation and Conduction Loss Corrections for the Pyrometer Measurements**

Temperatures of the burnt gas in the high-pressure burner are ~2000K. In this high temperature environment, radiation losses from the Pt/Rh bead used in the pyrometer measurements could be significant. The loss of energy via radiation could cause the bead temperature to be less than the actual gas temperature, resulting in lower measured values. In addition, conductive heat loss could occur via the extension wires attached to the bead and impact the measurements in the same way. To assess the potential error and correct for both the radiative and conductive losses, heat transfer analysis (energy balance) at the thermocouple bead is employed. The analysis involves three possible heat transfer modes at the bead–convection gain from the high temperature combustion gas, conduction loss to the extension wires, and radiation loss to the surroundings. If conduction loss from the extension wires is modeled as an infinite fin with a fixed temperature at the base [178], temperature loss is found to be less than 15K, and even smaller for our pyrometer setup where much of the wire is also exposed to the hot gas and along an isotherm. Therefore, the dominant energy transfer involves heat acquired through the convection process and the energy lost to the surroundings by radiation. Assuming the bead is spherical, the energy balance on the bead can be represented by the following equation.
where, $T_g$ is the corrected gas temperature (actual gas temperature), $T_b$ is the bead temperature (measured temperature), $T_\infty$ is the surrounding wall temperature, $\varepsilon_b$ is the emissivity of the platinum bead, $\sigma$ is the Stefan-Boltzmann constant, $D_b$ is the bead diameter, $Nu_D$ is the Nusselt number at the bead, and $k_g$ is the thermal conductivity of the gas at $T_g$. Emissivity of platinum higher than 1200K can be expressed as follows [179]

$$\varepsilon_b = 1.108 \times 10^{-4} T_b + 0.014.$$  

where, $T_b$ is the platinum bead temperature. The expression of the Nusselt number, $Nu_D$, for the flow over a sphere is can be expressed as [178]

$$Nu_D = 2 + (0.4 Re_D^{1/2} + 0.06 Re_D^{2/3}) Pr^4 \left( \frac{\mu}{\mu_s} \right)^{1/4}$$  

$$0.71 < Pr < 380, \quad 3.5 < Re_D < 76,000, \quad 1.0 < \left( \frac{\mu}{\mu_s} \right) < 3.2$$

where, $Re_D$ is the Reynolds number at the bead, $Pr$ is the Prandtl number, $\mu$ is the dynamic viscosity of the gas at the actual gas temperature, $T_g$, and $\mu_s$ is the dynamic viscosity of the gas at the bead temperature. The actual gas temperature should be used to calculate $Re_D$ and $Pr$. However, since the actual gas temperature is initially unknown, $T_b$ is used as an initial guess to estimate the Nusselt number. After obtaining the radiation loss, the corrected temperature is used to reevaluate $Nu_D$, and a new radiation loss. This iteration process is carried out until the radiation correction value converges ($\Delta T < 1K$). For the range of operating conditions in the high-pressure burner, the radiation corrections are between 80 and 120K.
Apart from the NO addition method used in this study, there are other ways to determine the baseline in applying the multi-line fitting. The baseline intensity can be extracted from the measured fluorescence emission spectra. As shown in Figure 6-8, different overlapping contributions from LIF signals of NO, O$_2$, CO$_2$ and elastically scattered laser light can be numerically separated. The intensities of simulated NO- and O$_2$-LIF emission spectra, experimental CO$_2$-LIF emission spectra and a Rayleigh-scattering signal can be simultaneously fit to wavelength-resolved experimental data via a non-linear least-square fitting procedure [114]. The background signal is then numerically integrated to yield the baseline intensity. While the NO addition approach is potentially applicable to 2-D imaging setups, a spectrally-resolved emission measurement is required for the emission spectra separation method, yielding at best 1-D information. Alternatively, the baseline can be determined from a direct fit to the LIFSim simulation where it is simply extracted from the multi-line fitting routine as a free parameter (as done in 1bar). Note this works well at 1bar, where the structure of the spectra is well defined. Because of pressure broadening at high-pressures ($p \geq$10bar), the scanned-excitation wavelength range no longer contains “off resonance” regions that allow the direct determination of background intensity and the numerical fitting of the baseline becomes unstable.

Comparison of baseline fraction (baseline signal/total signal) and subsequent temperatures for the different methods are shown in Table 6-1. Note that a shift in baseline intensity can produce a variation in the fit temperature even at pressures near 1bar. An increase of baseline with pressure can be observed for constant excitation wavelength ($\lambda_{ex}$=226.03nm), due to the increased contribution from hot O$_2$ and CO$_2$. For the NO addition method and the emission spectra separation, temperature differences are generally less than 70K and within error range of our thermometry method. However, baseline determination from direct multi-line fitting results in temperatures which exhibit more deviation and generally outside our error range. While the emission spectrum analysis cannot be applied to 2-D imaging measurements, baseline contribution can be determined at much higher pressures than the NO addition method, which is limited by the rapidly converging convergence lines (Figure 6-10) and can be useful in higher pressure regions where single point or 1-D line-resolved measurements are sufficient.
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Table 6-1 Comparison of baseline fraction (%) and resulting temperature from the NO addition method, emission spectra method and by direct baseline determination from multi-line fitting for different pressures. $\lambda_{ex}=226.034$nm. Temperatures are from multi-line fitting of excitation spectra with baseline determination from respective methods. NO addition method provides the highest accuracy.

6.5 2-D Temperature Imaging using Multi-Line NO-LIF Thermometry

Multi-line thermometry has the potential for 2-D imaging with an image recorded at each spectral position. As shown in Figure 6-14, this results in a stack of images with each image obtained at a specific wavelength in the excitation scan. This results in a three-dimensional data structure with two spatial axes and one excitation-wavelength axis. For each pixel (corresponding to local flame position), the LIF excitation spectrum is extracted along the wavelength axis and evaluated using multi-line thermometry. By fitting the excitation spectra using numerical simulations, the temperature at that pixel location can be obtained. In practice, this process is repeated for each pixel location and 2-D temperature fields then can be reconstructed from the individual fitting results. Higher pressure applications are complicated by the fact that baseline contribution must be determined for each pixel position, and an elaborate calculation routine must be implemented to extract baseline for each location inside the flame. 2-D temperature
fields obtained by using PLIF multi-line is fitting is shown in Figure 6-15 for various pressures in the Stanford high-pressure burner.

**Figure 6-14** Schematic of 2-D PLIF multi-line thermometry. Image is obtained at each wavelength position and excitation spectra can be reconstructed for each pixel location. Pixel by pixel fitting of the stack of excitation spectra yields 2-D temperature fields.

Using the 1-D line imaging, temperature profile along the path of the laser can also be obtained and a demonstration is shown in Figure 6-16 for 10, 20 and 40bar flames. The spatial resolution comes from our spectrometer alignment where the beam is parallel to the slit and thus provides a line resolved spectra in the direction of the laser. To account for the attenuation of the laser propagating through the medium, the baseline was separately determined for each individual spatial position using the NO addition method. The profiles show a plateau where the flat flame exhibits a constant temperature and rapid cooling near the edges. The co-flow air was not seeded with NO, therefore the cold outer regions were not accessible with the NO-LIF technique. The smooth temperature profiles illustrate the robustness of this thermometry method, as well as demonstrate the potential to provide accurate spatially resolved temperatures.
Figure 6-15 Temperature fields obtained using 2-D PLIF multi-line thermometry for various pressures (1–60bar).

Figure 6-16 1D spatial temperature profile along a horizontal line in the flame (3mm above burner matrix) for 10, 20 and 40bar. $\phi=0.9$ CH$_4$/air flame with 400ppm NO seeding.
6.6 Conclusion

A robust multi-line thermometry technique for 1-D and 2-D imaging application in steady high-pressure flames is presented along with the assessed accuracy of the method. Temperatures are reported in a stable, premixed methane/air flame ($\phi=0.9$) at pressures between 1–60 bar, and compared with an intrusive bead/pyrometer measurement for first order comparisons. The technique combines the measurement of NO-LIF signals within a pre-defined spectral range with fitting of simulated spectra using the flexible computational tool LIFSim. While computational modeling compensates for spectral overlap caused by strong collisional broadening, severe reduction of SNR ratio limits the technique to applications at $p \leq 50$ bar. The method yields absolute, quantitative temperatures without the aid of an external calibration. The experiment has confirmed the LIFSim spectral database needed to investigate potential strategies for fast imaging thermometry for high-pressure combustion applications. Potential applications include temperature validation for high-pressure flame chemistry and steady practical combustion systems. Multi-line fitting can also serve as a validation protocol for evaluating the accuracy and precision of the new strategies for fast-imaging thermometry in laboratory conditions.
Chapter 6
Chapter 7 Strategies for Multi-Window Detection of NO

In this chapter, measurements optimizing the multi-window (multi-wavelength) detection strategies of nitric oxide (NO) laser-induced-fluorescence (LIF) in high-pressure flames are presented. A single-laser, multi-camera detection strategy is proposed for isolation of the NO signal. This work builds on previous research that identified interference LIF from O\(_2\) and CO\(_2\) in high-pressure flames and optimized the choice of excitation strategies as a function of application conditions (Chapter 4). In this study, design rules are presented to optimize the LIF detection wavelengths for quantitative 2-D NO-LIF measurements over a wide range of pressures (1–60bar) and temperatures. Simultaneous detection of LIF in multiple wavelength regions enables correction of the NO signal for interference from O\(_2\) and CO\(_2\) and allows simultaneous imaging of all three species. Measurements of wavelength-resolved 1-D LIF in slightly lean (\(\phi=0.9\)) and slightly rich (\(\phi=1.1\)) methane/air flames are used to evaluate the design rules and estimate the NO detection limits for a wide range of flame conditions. The quantitative 2-D measurements of NO in the burnt gas are compared with model calculations (using GRI-Mech 3.0) versus pressure for slightly lean and slightly rich flames. The discussions and demonstrations reported in this study provide a practical guideline for application of instantaneous 1-D or 2-D NO-LIF imaging strategies in high-pressure combustion systems.

7.1 Background

7.1.1 Interpretation and Quantification of NO PLIF imaging

The conversion of measured NO PLIF intensities to quantitative concentrations requires correction for inhomogeneities in the laser sheet, attenuation of the probe beam and fluorescence signal, influence of temperature, pressure, and the concentrations of all
other species, as well as the knowledge of the influence of these factors on the NO spectroscopy [1]. We refer to such corrected PLIF images as “semi-quantitative”. Furthermore, calibration of the corrected LIF intensities to absolute number densities or mole fractions is required for quantitative NO concentration measurements, accounting for the influence of collection optics, detector quantum efficiency, laser energy density, etc.

The main temperature influence on the NO-LIF signal strength arises from the ground state population of the laser-coupled levels. Furthermore, temperature, pressure, and gas phase composition affect the frequency and cross section of collisions that an NO molecule encounters. This influences both the excitation efficiency and the fluorescence quantum yield. Collisional (pressure) broadening and line-shifting have been measured for the NO molecule for the collisions with main combustion species [20-23]. A variation in pressure, temperature, and (to a minor part) gas phase composition influences the spectral overlap of the laser with the NO absorption features. As a result, excitation efficiency and therefore LIF signal decreases with increasing pressure. Collisional fluorescence quenching of the NO $A$ state has been investigated in detail [180-183], and models have been set up to describe the effects of temperature and colliding species on quenching cross sections [95, 97, 184]. The quenching rate is proportional to pressure. Fluorescence quantum yield and therefore LIF signal decrease strongly with increasing pressure, and further vary with temperature and gas composition.

Pressure can be measured accurately in most situations and with high temporal resolution using piezoelectric sensors. Therefore, the correction of the LIF signals for pressure is relatively simple to carry out. The measurement of temperature, on the other hand, requires a large experimental effort, and it is usually very difficult to obtain temperature information simultaneously with NO-LIF imaging data in practical, often turbulent flows. While calculated estimations of temperature can be used for correction of the LIF intensity, the accuracy is severely limited in unsteady flames. Thus, quantitative NO concentration measurements without the exact knowledge of local temperature often require choosing a transition which minimizes the total temperature sensitivity of the LIF signal. In some cases a systematic variation of the ground state population with temperature may be desired to compensate for other temperature-
dependent effects.

Even less available than temperature is the concentration of colliding species. While chemical simulations are feasible in laminar flames [185], NO LIF in turbulent combustion situations normally cannot be corrected for. The introduced error is, however, relatively small for premixed combustion since NO is present only in the post-flame-front gases where the majority species concentrations are known relatively well.

### 7.1.2 Goal of Current NO-PLIF Imaging Strategy

The scope of research for investigation of a single-laser, multi-camera detection strategy for fast imaging of NO LIF in practical combustion systems is presented in this section. In Chapter 4, a comprehensive study of quantitative NO-LIF in flames for pressures up to 60bar was presented, leading to enhanced understanding of high-pressure NO-LIF. In this previous work, different excitation strategies were investigated and optimized excitation wavelengths for NO-LIF were recommended for various combustion environments [104-106].

The aim of the present study is to optimize the detection strategy for quantitative 2-D NO-LIF imaging. This work builds on the results of the previous studies of high-pressure NO-LIF (Chapter 4), and leads to a new strategy based on the use of multiple detection wavelength regions for simultaneous determination of NO and the interference from O₂ and CO₂ LIF. Design rules are developed and the detection wavelength regions or “windows” are optimized, using new wavelength-resolved 1-D NO-LIF experiments in slightly fuel lean (ϕ=0.9) and slightly fuel rich (ϕ=1.1) methane/air flames. Demonstration measurements of 2-D LIF imaging are then performed to validate the imaging strategy and estimate the NO detection limits for lean and rich high-pressure flames. In addition, quantitative measurements of NO in these seeded flames are compared with detailed chemical kinetics calculations as a function of pressure and stoichiometry. While the reaction mechanism used in the simulations are not optimized for high-pressure applications, fairly good agreement was observed for the NO formation in the burnt gases as the simulations captured the trend of the pressure dependence.
Chapter 7

7.2 Experiment

The high-pressure burner used in this study has been previously described (Chapter 3.1) and investigations were conducted for equivalence ratios of $\phi=0.9$ and 1.1 in methane/air flames over a pressure range of 1–60 bar. Laser pulse energy ranged from 0.8–1.2 mJ/pulse (7 ns pulse at 10 Hz with linewidth of 0.2 cm$^{-1}$) from a Nd:YAG-pumped (Quanta Ray GCR250) frequency-doubled (BBO) dye laser (LAS, LDL205).

![Diagram of experimental setup]

**Figure 7-1** Experimental setup for spectrally dispersed 1-D line-imaging (upper panel, left section) and spatially resolved 2-D imaging (upper panel, right section). Lower panel shows concept of multi-window detection scheme for practical applications.

For spectrally resolved 1-D line-imaging measurements, the beam was weakly focused (diameter=1 mm) along a line 3 mm above the burner matrix and crosses the flame horizontally (Figure 7-1, upper panel, left side). The pulse energy was monitored with a fast photodiode (LaVision). Fluorescence signals were collected at right angles to the laser beam and focused with a $f=105$ mm, $f/4.5$ achromatic UV-lens (Nikon), dispersed spectrally through an imaging spectrometer (LaVision Chromex 250IS) and imaged onto an intensified CCD camera (LaVision Dynamight). For 2-D imaging measurements, the laser was optically stretched into a vertical sheet (0.5 mm×15 mm) and imaged directly
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using an ICCD camera with different filter sets for suppression of Rayleigh Scattering and bandpass filtering (Figure 7-1, upper panel, right side). The signals from 20 laser pulses were accumulated on chip for all measurements. For multi-window imaging measurements, wavelength regions were isolated with bandpass filters (discussed below) and separately collected on a single camera. For practical 2-D imaging applications where all spectral windows require simultaneous detection, a single laser, multi-camera strategy is proposed as shown in the lower section of Figure 7-1.

7.3 Measurement Strategy

7.3.1 High-Pressure Issues with Fast NO-LIF Imaging

A more detailed discussion regarding problems caused by elevated pressure in LIF measurements were previously presented in Chapter 4.1.2, and only a brief summary is presented here with a focus on fast imaging of NO. There are three significant complications that arise when applying NO-LIF to high-pressure combustion environments: (1) pressure broadening and shifting of NO transitions, (2) strong attenuation of UV light and (3) interference LIF. Excitation features of NO broaden with increased pressure, and for pressures greater than 10bar, it is no longer possible to excite single rotational features of the excitation spectrum due to the spectral overlap [104].

Along with an increase in fluorescence quenching of the NO A state, pressure broadening leads to a decrease in the overall signal strength since the laser linewidth (0.25cm$^{-1}$) is less than the broadened linewidths. Second is the strong attenuation effect of both the excitation laser light and fluorescence signal. UV light at short wavelengths (<250nm) is strongly absorbed in hot post-combustion gases, due mainly to strong absorption by CO$_2$ and H$_2$O [109, 110] (CO$_2$ being the more dominant contributor in our wavelength range and temperatures). This effect increases with pressure as densities of the absorbing species increase. Finally, there can be significant signal interference. The $B^1\Sigma^+ - X^3\Sigma^+$ Schumann-Runge bands of O$_2$ are pervasive in the same excitation and detection region and can be a major interference source in fuel lean and non-premixed flames [8]. Recently identified CO$_2$ broadband fluorescent emission (200–450nm) is also a concern.
in high-pressure flames [114]. Additionally, polycyclic aromatic hydrocarbon (PAH) LIF emission can be a source of significant interference in fuel rich flames.

From a practical point of applying fast NO-LIF imaging, pressure broadening and attenuation effects lead to decrease of the overall signal and higher laser powers are required to ensure sufficient SNR ratios during single pulse excitation of NO.

![Emission Spectra of NO-LIF with 226.03nm Excitation (40bar flame, \( \phi = 0.9 \), 300ppm NO seeding). Spectra was obtained by taking 1-D line-imaging (top box). NO, O\(_2\) and CO\(_2\) emission profiles are enhanced for clarity (bottom 3 boxes). W1, W2 and W3 indicate the detection windows. Profiles were taken in a 1mm region in the center of the flame.](image)

**Figure 7-2** Emission Spectra of NO-LIF with 226.03nm Excitation (40bar flame, \( \phi = 0.9 \), 300ppm NO seeding). Spectra was obtained by taking 1-D line-imaging (top box). NO, O\(_2\) and CO\(_2\) emission profiles are enhanced for clarity (bottom 3 boxes). W1, W2 and W3 indicate the detection windows. Profiles were taken in a 1mm region in the center of the flame.

### 7.3.2 2-D Imaging of NO using Multi-Wavelength Detection

Isolation of NO-LIF signal from interference sources, mainly from LIF of hot O\(_2\) and CO\(_2\) is investigated using LIF detection in multiple wavelength windows. For practical imaging applications, most combustion systems fluctuating cycle to cycle and frequently with turbulent flow fields require a fast imaging strategy where single shot or multiple shots are executed within a short time duration to capture the instantaneous distribution of species. While the ultimate goal would be the development of a single-
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shot 2-D imaging strategy, all the data presented here are obtained by accumulating multiple laser pulses on an ICCD camera (20shots/image), made possible by the steady nature of the test flame in the Stanford high-pressure burner. By averaging over multiple laser pulses, it is possible to estimate the single-shot LIF signals achievable using lasers above the modest power range (0.8–1.2mJ/pulse) of the experimental setup.

Figure 7-2 shows a typical emission spectrum of NO-LIF using 1-D imaging with $A-X(0,0)$ band excitation, where non-linear fitting and computational simulation of NO, O$_2$ and CO$_2$ LIF emission [10] are used to separate the spectrum into components from NO, O$_2$, and CO$_2$ LIF, and the Rayleigh scattering of the laser. It can be seen that O$_2$ and CO$_2$ LIF are emitted throughout the entire region of interest and overlap with the spectral features of NO. Details regarding the selection criteria for the wavelength windows in Figure 7-2 (W1, W2 and W3) will be discussed later in section 7.4 (‘Results and Discussions’).

7.3.3 Data Evaluation

The specific steps for high-pressure 2-D LIF image analysis are discussed. The raw images first are corrected for spherical aberration of the collection lens (Lavision ‘Davis’ Distortion Correction Routine) and for any non-uniform energy distribution of the laser sheet by using an averaged LIF image of the burner flooded with NO. For each detection window, the signal at each pixel is the sum of contributions from NO, O$_2$ and CO$_2$ LIF. The fluorescence spectrum of each molecule is well-known [10, 114] and provides the relative LIF signal strength for a particular molecule in the three detection windows. This knowledge, coupled with relative detection efficiencies of the filters in each window, allows us to solve for the NO, O$_2$ and CO$_2$ mole fractions. Pixel-by-pixel solution enables reconstruction of the LIF images for all species. It should be noted that the relative collection efficiency in the different detection windows for all three species involved is not a function of temperature. Collisional redistribution of the excited upper state can in principle produce a temperature dependence of the collection efficiency for the different detection windows. However, the collisional quenching and the redistribution of the population due to rotational energy transfer (RET) both scale
linearly with pressure and there is negligible increase of rotational energy redistribution as a function of pressure within the allowed fluorescence lifetime.

![Flame Configuration](image)

**Figure 7-3** Signal attenuation (%) by CO$_2$ and H$_2$O absorption for a $\phi=0.9$ flame at various pressures.

The images are then corrected for attenuation of the excitation laser light and fluorescence signal, which is dominated by absorption from hot CO$_2$ with a small contribution from hot H$_2$O; note that absorption contributions from NO and O$_2$ are negligible in the flames studied here. Attenuation of the laser light and fluorescence signal are corrected on a pixel-by-pixel basis using Beer-Lambert’s Law and absorption coefficients known from shock tube measurements [109] and simple consideration of the geometry. These corrections require some knowledge of the local temperature because the CO$_2$ and H$_2$O absorption coefficients are temperature dependent and the CO$_2$ and H$_2$O number densities are obtained using an assumption of thermal equilibrium in the post-flame gas. The effects of laser beam and signal attenuation by CO$_2$ and H$_2$O absorption are shown in Figure 7-3, where the attenuation (%) is plotted for a $\phi=0.9$
strategies for multi-window detection of NO flame at various pressures. Quantitative temperature fields used for the attenuation correction were obtained by 2-D 2-line NO-LIF thermometry [159] (line selection: 226.03nm and 225.847nm) and are shown in Figure 7-4.

![Figure 7-4](image)

Temperature information is also needed to correct for the temperature variation of the NO-LIF signal via the temperature dependence of the laser-excited ground state population, the spectral overlap between the laser-spectral profile and NO absorption spectrum, and the fluorescence yield. These corrections for NO-LIF temperature dependence are small for the excitation wavelength used, and only an estimate would be needed for single-shot 2-D imaging applications. This is an important issue in practical applications of NO-PLIF imaging, were simultaneous imaging of both NO and temperature fields are often difficult and estimations of temperature from numerical modeling must be used. Once again, quantitative temperature fields shown in Figure 7-4 (obtained using 2-D 2-line NO-LIF thermometry [159]) was used for these corrections. For actual detection of NO concentrations in this work, an excitation wavelength of 226.03nm that excites lines \( P_1(23.5), Q_1+P_{21}(14.5), Q_2+R_{12}(20.5) \) in the \( A-X(0,0) \) band was used. This wavelength has been previously identified as optimal for maximum NO signal strength and minimum interference from \( O_2 \)-LIF [8, 105] (Chapter 4, “DiRosa Line”).
7.3.4 Spectrally Resolved Line-Imaging of NO

Spectrally resolved 1-D line-imaging is obtained by aligning the laser beam parallel to the spectrometer slit, and the LIF signal is dispersed onto an ICCD camera. This camera image (top box in Figure 7-2), has the position along the laser beam on the ordinate and the fluorescence wavelength on the abscissa. A schematic of the overall setup for 1-D line-imaging was previously shown in Figure 3-8. 1-D line-imaging provides increased SNR ratio due to higher laser intensity (beam vs. sheet), direct visualization of interference sources, and a more flexible selection of excitation/detection strategies since NO-LIF can be easily isolated from interferences.

![Figure 7-5](image)

**Figure 7-5** Simulated 40bar emission spectra with low NO concentration (~25ppm). NO-LIF intensity is scaled using quantitative values obtained from this study. This method is applicable along a line in the path of the laser (1-D line-imaging).

In addition, only a single laser and single camera detection setup is required. Due to these advantages, 1-D line-imaging itself is an attractive detection strategy when 2-D information of concentration field is not required and the information along the line of the laser is sufficient. In particular, the high SNR of 1-D line-imaging and the added benefit of monitoring multiple emission features of NO-LIF simultaneously offer high
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sensitivity to extremely low concentrations of NO (<25ppm). The spectrally resolved 1-D imaging spectra used in this study can be modified to predict performance at lower NO concentrations by scaling the NO intensity and monitoring the decrease in the SNR ratio.

Figure 7-5 shows a simulated fluorescence spectrum at 40bar with a low (25ppm) level of NO at a typical flame temperature of ~2000K. NO-LIF features are clearly visible, although significant interference from O$_2$ and CO$_2$ can also be observed. Further studies are required to identify the actual limits of detectable NO levels using 1-D line-imaging, while projections using simulations as in Figure 7-5 show that concentrations below 10ppm may be possible. Note that interference from PAHs or particles pose only a slight decrease in the detection limit since signals can be visually separated from each other using spectrally resolved 1-D line-imaging.

Previous demonstrations of 1-D line-imaging in both laboratory flames [104] and practical combustors [76] can be found in the literature. To date, very few studies have actually utilized 1-D line imaging as the primary detection strategy but more as a reference for monitoring the emission from different combustion species. Similarly, for the PLIF imaging work presented in this section, 1-D line-imaging provides the guideline for selection of the individual detection windows by monitoring the spectrally resolved emission from all the relevant species (NO, O$_2$ and CO$_2$). Nonetheless, 1-D line-imaging holds much potential as a detection strategy capable of providing very high sensitivity and accuracy.

7.3.5 Saturation and Laser Intensity

With modern-day high-power, short pulse (<10ns) lasers, LIF signal dependence on laser energy can show non-linear effects due to saturation of the excitation transition. In our 1-D line imaging experiments, we observed only a slight deviation from linear excitation when the laser spectral intensity ($I_\nu$) reached ~30W/m$^2$s$^{-1}$ (1mJ, 7ns pulse @ 226.03nm with 0.2cm$^{-1}$ bandwidth and a focused diameter of 1mm) in an atmospheric pressure flame. As pressure is increased to the pressures of current interest, the rapid increase in the rotational energy transfer refills the depleted ground state while removing excess population in the upper excited state, thereby greatly extending the linear regime of NO-LIF. This population recycling effect enables the use of higher laser power for
linear single-shot imaging in high-pressure environments (e.g., up to 20mJ/pulse @ 20bar for our setup) resulting in increased SNR ratios. For 2-D imaging measurements, significantly stronger laser pulses can be used since the laser beam is dispersed into a sheet and the spectral intensity is decreased.

7.4 Results and Discussions

7.4.1 Detection Wavelength Window Selection

Figure 7-2 shows the detection windows used for the 2-D imaging measurements (W1, W2 and W3) used in this study. The basic concept involves having a primary window for detection of NO and addition windows for correction of interference from other species. Window 1 (254nm, FWHM 17.5nm; Asahi Optics) is the primary detection channel for NO, chosen to optimize the NO LIF signal, while window 2 (280nm, FWHM 12nm; Lambda Research Optics) and Window 3 (340nm, FWHM 10nm; Asahi Optics) are used to correct the signal for interference from O$_2$ and CO$_2$, respectively. In addition, a 240nm long-pass filter was used for additional suppression of the Rayleigh scattering.

The selection rules for W1, the primary NO-LIF detection window, maximize the selectivity and intensity, while minimizing the contribution from Rayleigh scattering of the laser. The bandpass width should also be wide enough to avoid bias in the collection efficiency depending on the rotational levels excited [115]. For our test flame, optimization was carried out by taking the spectrally resolved line-imaged data (Figure 7-2) and scanning a simulated Gaussian filter function (with varying spectral widths) throughout the fluorescence spectrum.

An example from a 40bar, $\phi=0.9$ flame is shown in Figure 7-6 for various excitation strategies and detection spectral widths, where the signal purity (fraction of the LIF signal from NO) and relative NO-LIF intensity are plotted as a function of center wavelength of the simulated filter. Mainly two detection windows (7nm and 17nm) which correspond to detection of either one or two vibrational bands of NO in the emission spectrum, are investigated.
Figure 7-6 Optimization of primary detection window W1 with $A-X(0,0)$, $(0,1)$ and $(0,2)$ excitation (40bar, $\phi=0.9$ flame, 300ppm NO seeding). Signal purity (fraction of LIF signal from NO) and relative NO-LIF intensity are plotted as a function of a simulated Gaussian filter function center wavelength (FWHM=7 and 17nm). For $A-X(0,0)$ excitation, maximum signal purity and NO-LIF intensity can be obtained at a center wavelength of 254nm.
For detection windows W2 and W3, which are used to isolate interference LIF, the selection criteria require regions with maximum fractional contribution from the specific interference species for increased accuracy in the correction.

While the 2-D imaging measurements reported in this paper primarily use the $A-X(0,0)$ transition at 226.03nm, optimization of the primary NO detection window W1 was also carried out for excitation using the $A-X(0,1)$ and (0,2) transitions (235.873 and 247.941nm) as shown in Figure 7-6, and the optimized results are presented in Table 7-1. Note that excitation using $A-X(0,1)$ and (0,2) transitions offer the possibility of selecting W1 blue-shifted of the laser to avoid interference signals that occur at predominantly longer wavelengths. Also note that red-shifted detection of $A-X(0,2)$ excitation suffers from severe interference (very low NO fraction as shown in Figure 7-6) and is not recommended. The same values for the detection windows W2 and W3 are recommended for all excitation strategies, as these windows are used to isolate $O_2$ and $CO_2$ respectively.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Center $\lambda$</th>
<th>FWHM</th>
<th>Emission Bands</th>
<th>Purity</th>
<th>Rayleigh</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A-X(0,0)$ 226nm</td>
<td>253</td>
<td>17</td>
<td>$A-X(0,2),(0,3)$</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>$A-X(0,1)$ 235nm</td>
<td>226</td>
<td>8</td>
<td>$A-X(0,0)$</td>
<td>0.90</td>
<td>yes</td>
</tr>
<tr>
<td>$A-X(0,1)$ 235nm</td>
<td>253</td>
<td>17</td>
<td>$A-X(0,2),(0,3)$</td>
<td>0.83</td>
<td>yes</td>
</tr>
<tr>
<td>$A-X(0,1)$ 235nm</td>
<td>264</td>
<td>17</td>
<td>$A-X(0,3),(0,4)$</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>$A-X(0,2)$ 248nm</td>
<td>226</td>
<td>10</td>
<td>$A-X(0,0)$</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>$A-X(0,2)$ 248nm</td>
<td>235</td>
<td>8</td>
<td>$A-X(0,1)$</td>
<td>0.80</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 7-1 Optimized selection for primary detection window W1 for $A-X(0,0)$, (0,1) and (0,2) transitions. Purity is the fraction of NO-LIF Signal from the total signal (NO-LIF signal/Total). Rayleigh refers to emission regions which may be subject to interference from Rayleigh scattering of the laser.

Selection of the optimum number of detection wavelength windows requires knowledge regarding the global chemistry of the combustion process involved. For many experimental applications, single-window detection (W1) is sufficient as the flames have minimal $O_2$ and $CO_2$ interference if the proper excitation and fluorescence wavelengths
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are selected. Non-sooting flames with equivalence ratios near one or slightly richer, generally exhibit negligible levels of signals from O₂, and contribution from CO₂ LIF can also be neglected for pressures less than 20bar. For high-pressure flames (≥20bar) with lean chemistry (φ<0.9), the interference from CO₂ and O₂ requires more than one detection window for sensitive and accurate detection of NO. In the case of rich flames (φ>1.5) or flames with incomplete combustion of the fuel, interference from PAH and other hydrocarbons can additionally complicate NO-LIF measurements and will require further work to establish an appropriate detection strategy.

Figure 7-7 NO addition plots for calibration of LIF intensity (20 and 40bar flames, φ=0.9, 300ppm NO seeding). Convergence point of two linear lines (fits to two excitation wavelength, λ_A at 226.03nm and λ_B at 226.042nm) indicates mole fraction of nascent NO formation and corresponding LIF Intensity.

7.4.2 NO Addition Method for Quantitative NO Detection

Calibration of NO-LIF intensities for 2-D imaging often requires an additional measurement [68]. In practical applications such as engine measurements, a well-characterized calibration flame may be inserted into the field of view for direct calibration of NO-LIF intensities [186]. This type of in-situ calibration using NO addition involves varying the amount of seeded NO and monitoring the change in the intensity of NO-LIF. Premixed lean flames are preferred to minimize NO reburn [68] in fuel rich-regions and to ensure that reburn rates depend linearly on seeding amounts. For
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the work presented here, NO-LIF signals are calibrated using an NO addition method previously introduced in Chapter 6.

NO is excited at two different wavelength positions ($\lambda_A : 226.03\text{nm}$ and $\lambda_B : 226.042\text{nm}$) and concentration is varied from 200 to 600ppm in 100ppm intervals as shown in Figure 7-7 for 20 and 40bar flames with $\phi=0.9$. Two linear fits to the data cross in the lower left corner and provide information regarding nascent NO formation of the flame and NO LIF calibration. While the two-line NO addition method has the benefit of providing nascent NO concentrations and increased accuracy at moderate pressures, the convergence point of the lines becomes hard to determine at pressures exceeding 60bar as the lines collapse onto each other. However, once the intensity is calibrated for a specific condition (preferably at 10 or 20bar where line convergence is easy to determine), other pressures can be easily corrected for by using relative signal strengths and pressure and temperature dependence relations.

7.4.3 Multi-Window 2-D Imaging of NO

Accurate 2-D NO-LIF images require corrections for various effects including laser and fluorescence signal attenuation, which vary with gas temperature. For steady laboratory flames, time consuming strategies such as multi-line NO-LIF fitting [116] can be used to obtain accurate 2-D temperature fields. For practical applications, 2-line thermometry offers a rapid means to obtain 2-D temperature images with relatively high precision. The temperature fields used in this study are obtained via 2-D 2-line thermometry of NO-LIF (line selection: 226.03nm and 225.847nm) and are were previously shown in Figure 7-4. A detection window centered at 254nm (FWHM 17.5nm; Asahi Optics) was used to maximize the signal purity of the NO-LIF.

Quantitative 2-D NO-LIF images obtained from the multi-window detection strategy are shown in Figure 7-8. The data in Figure 7-8 show that for slightly lean flames ($\phi=0.9$), NO concentrations increase with pressure as predicted by the thermal and prompt NO formation mechanisms [6]. For slightly rich conditions ($\phi=1.1$), NO reburn due to excess hydrocarbons in the flame causes the concentrations to decrease with pressure. A comparison of relative NO concentrations for various conditions with
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Model calculations using the PREMIX code and GRI-Mech 3.0 reaction mechanism is presented in the following chapters.

Figure 7-8 Quantitative NO concentrations from multi-window 2-D NO-LIF Imaging (1–60bar, \( \phi = 0.9 \) and 1.1 with 300ppm NO seeding). Note that the NO concentrations in rich flames are significantly reduced by NO reburn.

Figure 7-9 O\(_2\) and CO\(_2\) concentration fields from a three-window 2-D imaging strategy applied in a 40bar flame (\( \phi = 0.9 \) and 1.1 with 300ppm NO seeding). LIF Intensities are calibrated using Chemkin Premix 1-D flame calculations.

The data at pressures of 1 and 10bar use a two-window (W1 & W2) detection since interference from CO\(_2\) is negligible under these conditions [114]. The second window provides a means to correct the raw image for the interference of O\(_2\)-LIF in
slightly lean conditions ($\phi=0.9$). In slightly rich conditions ($\phi=1.1$), O$_2$ is mostly consumed during the reaction and single-window (W1) detection is sufficient (NO-LIF signal selectivity>98%) and no correction is needed. For pressures of 20bar and higher, a three-window detection strategy is used for correction of the raw images for both O$_2$ and CO$_2$ LIF. The additional windows allow simultaneous images of hot CO$_2$ and O$_2$. The data in Figure 7-9 show these O$_2$ and CO$_2$ interference images for rich and lean 40bar flames. While both O$_2$ and CO$_2$ images have been corrected for temperature dependence of the LIF signal, the literature on their temperature dependence is not as complete as that of NO, resulting in a decrease of accuracy across the image field. Quantitative calibration for the two species were carried out at a point just above the initial flame front and by using the results obtained from Chemkin Premix 1-D flame calculations.

7.4.4 Pressure Dependence of NO-LIF SNR

Spectrally resolved 1-D line-imaging offers unique advantages in applying single-shot detection of NO-LIF to practical systems. In the current work, 1-D line-imaging measurements were carried out for all flame pressures (1–60bar) and stoichiometry to provide guidelines for filter selection in the multi-window detection strategies used for 2-D measurements. These 1-D measurements do not require the laser beam to be spread into a sheet, and the higher laser energy intensity results in increased SNR. A comparison of SNR for 1-D line and 2-D imaging data for 1mJ laser energy used in the current study are presented in Figure 7-10 for 300ppm NO seeding.

The curves in Figure 7-10 were calibrated using data taken with 20 shots accumulated on chip and extended to other values using statistical arguments for this shot-noise-limited case. Averaging 20 shots is equivalent for our experimental setup to single-pulse laser energy of ~20mJ, a value generally recommended for single-shot 2-D imaging applications to achieve SNR of ~10 at pressures exceeding 40bar (assuming laser sheet of 0.5mm×15mm). Commercially available optical parametric oscillators (OPO), tunable KrF excimer laser (~248nm) or sum frequency mixing dye lasers (SFM) are capable of supplying laser energy in this range, and as discussed above the excitation is well below saturation at elevated pressures.
Figure 7-10 Comparison of SNR for spectrally resolved 1-D imaging and 2-D imaging of NO-LIF for pressure conditions presented in this study (1−60bar) and as a function of shots accumulated on chip (1mJ/pulse).

7.5 Computational Simulations using GRI-Mech 3.0 (PREMIX)

The quantitative NO LIF data allows us to compare measurements of NO concentrations in the burnt gases with model calculations. Due to the geometry of the flat flame stabilized on a flat circular matrix, the reaction zone and post combustion gas region in the center of the flame can be effectively modeled as a 1-D flame. The modeling was carried out using Chemkin and Premix from Reaction Design with the reaction mechanisms supplied by GRI-Mech 3.0. The Premix code involves solving a set of governing differential equations that describe the flame dynamics using implicit finite difference methods, as well as a combination of time-dependent and steady-state methods. The solver algorithm employed automates coarse-to-fine grid refinement as a means to enhance the convergence properties of the steady-state approach and as a means to provide optimal mesh placement. The computational time for one specific NO concentration profile is approximately 3−5 minutes on a Pentium III 2.7GHz, depending on pressure and stoichiometry.
Figure 7-11 Comparison of NO Concentrations 3mm above the burner matrix with Chemkin Premix 1-D flame code (GRI-Mech 3.0) as a function of pressure and equivalence ratio ($\phi=0.9$ and $\phi=1.1$) with 300ppm NO seeding. Arrowhead markers show simulations using temperature profiles scaled ±50K.

Figure 7-11 shows a comparison of NO concentrations (3mm above the burner surface) obtained from NO-LIF imaging and Premix calculations for two equivalence ratios, $\phi=0.9$ and $\phi=1.1$. The calculations presented here were performed by specifying gas temperature profiles corresponding to those extracted from the 2-line NO-PLIF thermometry measurements (Figure 7-4). Using this option, the energy equation becomes redundant and is not used in the solution. By specifying the temperature profile, the heat transfer effects near the burner matrix, which are difficult to implement in the model, are taken into consideration. The relevant transport properties (thermal conduction and diffusion coefficients) and transport coefficients for individual species are calculated from tabulated intermolecular potentials and mixture-averaged-formulations (as opposed to multicomponent formulations) are used.

The arrowhead markers on Figure 7-11 show simulation results using temperature profiles scaled ±50K of the original peak value to demonstrate the
Strategies for Multi-Window Detection of NO

temperature dependence of the calculations. While Premix calculates the propagation of combustion as a function of axial distance, only single point (3mm above burner surface) comparisons are presented in this study. This is due to the fact that temperature profiles and concentrations are inaccurate in the obtained images very close to the matrix due to the cutoff of the laser sheet. In addition, axial distances above 3mm are affected by instabilities, decreasing the temperature due to diffusion of the coflow. Therefore, 1-D flame assumptions are inadequate for axial distances greater than ~5mm.

It can be seen from Figure 7-11 that formation of NO is strongly dependent on temperature for lean flames, while rich flames exhibit less dependence. This is due to the dominant effects of the Zeldovich mechanism [176] (otherwise known as thermal NO) in lean stoichiometries, while mechanisms for NO reburn chemistry prevail in the rich case. Therefore, for fuel-lean conditions, it is extremely critical to conduct simulations using highly accurate temperature profiles. On the other hand, for fuel rich conditions, the role of $C_1/C_2$ and $C_3^+$ chemistries become significant as the role of NO reburn is increased and this part of the chemical mechanism is less temperature dependent. For the results presented in Figure 7-11, discrepancies between the measured and modeled NO concentrations can be observed for higher pressures ($p>20$bar) in both lean and rich cases. However, all the LIF data correlates well with the model values when uncertainties in the temperature profile ($\pm50K$) are considered.

Figure 7-12 shows the same comparison made between seeded NO flames (300ppm) and unseeded fuel-lean flames. For unseeded flames, NO production comes strictly from nitrogen molecules in the air. For both cases, the NO formation is mainly driven by the Zeldovich mechanism and strong dependence of the simulation on temperature is observed. In a $20$bar $\phi=0.9$ flame, thermal NO accounts for about 82% of the total production, which was determined by turning off the rate-controlling reaction in the thermal mechanism ($N_2+O\leftrightarrow NO+N$) in GRI-Mech 3.0 during the simulation and monitoring the relative NO formation. A brief overview of NO formation mechanisms and pressure dependence are summarized in Appendix 2. While the LIF data in Figure 7-12 show good correlation with the simulation results within the model variation with a temperature uncertainty of $\pm50K$, very precise temperature profiles would be required to conduct an accurate assessment of the model chemistry.
Figure 7-12 Comparison of NO Concentrations 3mm above the burner matrix with Chemkin Premix 1-D flame code (GRI-Mech 3.0) as a function of pressure for 300ppm NO seeding and with no NO seeding ($\phi=0.9$). Arrowhead markers show simulations using temperature profiles scaled $\pm50K$.

Temperature and NO concentration profiles for a sample simulation in a 20bar CH$_4$/air fuel-lean flame are shown in Figure 7-13. The temperature profile shown in the top panel is extracted from the 2-line NO-PLIF thermometry measurements (Figure 7-4). As can be seen from Figure 7-13, the temperature profile extends down to 1mm above the burner matrix, limited by the edges of the laser sheet in the PLIF setup. The temperature profile within the burner surface and the 1mm region is extrapolated to the matrix surface (dotted line). The two lower panels are NO concentration profiles as a function of distance from the burner surface. Additional profiles also show simulations using peak temperatures scaled $\pm50K$ to demonstrate the temperature sensitivity. NO concentration data from LIF and simulated value at the 3mm mark are additionally plotted for reference. It can be seen that significant NO formation occurs after temperatures in excess of 1500K are reached, providing further verification that the thermal NO formation is the dominant mechanism.
A notable observation from the NO concentration profile in the seeded flame is that just before the reaction zone, a fraction of the NO experiences a rapid conversion to NO$_2$, only to be fully and rapidly converted back to NO. A sharp dip in the concentration profile can be seen as a result. This rapidly coupled reburn and formation process of NO is mainly due to the concentration of HO$_2$ radicals in the flame resulting from the initial pyrolysis of the fuel. Generally for fuel-lean flames, this is followed by additional formation of NO through the Zeldovich mechanism as can be observed in the 300ppm case (bottom plot).
Chapter 7

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \text{ (NO}_2 \text{ conversion)}, \\
\text{NO}_2 + \text{H} & \rightarrow \text{NO} + \text{OH}, \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2.
\end{align*}
\] (7.1)

7.6 Conclusion

A strategy for selective and quantitative LIF detection of NO in high-pressure combustion environments using spectrally resolved 1-D imaging and spatially resolved 2-D imaging (i.e., PLIF) was investigated. A 2-D NO-LIF imaging strategy for high-pressure detection was proposed and demonstrated using multiple wavelength windows. Spectrally resolved 1-D line-imaging was used to identify the sources of interference and provide guidelines for selecting filters in the multi-window strategy. 2-D imaging of NO-LIF was demonstrated by using \( A-X(0,0) \) excitation (226.03nm) with multi-window detection to correct for interference effects from other species (\( \text{O}_2 \) and \( \text{CO}_2 \)) in slightly lean and rich conditions (\( \phi=0.9 \) and 1.1). In addition to quantitative imaging of NO concentrations, the simultaneous imaging of the interference species \( \text{O}_2 \) and \( \text{CO}_2 \) is demonstrated. Spectrally resolved 1-D line-imaging offers the possibility of highly selective detection of NO-LIF down to extremely low concentrations (<10ppm) with only a one-laser and one-camera setup. In addition, the measured NO concentrations are compared with model calculations using Chemkin and Premix with GRI-Mech 3.0. The calculations were able to capture the trend of NO formation as a function of pressure for flames with both seeded and unseeded NO. The discussions and demonstrations reported in this study provide a practical guideline for application of instantaneous 1-D or 2-D NO-LIF imaging in high-pressure combustion systems.
Chapter 8 Conclusion

A comprehensive study to develop practical diagnostic strategies for detection of temperature and nitric oxide (NO) in high pressure ($p<60\text{bar}$) combustion systems using Laser-Induced-Fluorescence (LIF) was presented in this dissertation. The motivation for this study stems from the fact that NO-LIF, when applied to elevated pressures, suffers from a decrease of signal due to pressure broadening, overlapping of the excitation lines, attenuation of the propagating laser beam/fluorescence signal and interference from other species (mainly $\text{O}_2$ and $\text{CO}_2$). A comprehensive study of NO-LIF in a laboratory high-pressure flame was presented for various flame stoichiometries, pressures and excitation wavelengths to develop optimized strategies for application of NO-LIF in practical high-pressure combustion systems. Four main conclusions can be drawn from this study.

First, optimizations of excitation strategies for high-pressure applications in the $A^2\Sigma^+ - X^2\Pi$ $(0,0)$, $(0,1)$ and $(0,2)$ bands of NO were carried out and performance of various excitation wavelengths were compared in order to provide guidelines for selecting an optimized strategy for a specific combustion condition. The comparison took into account the influence of signal strength, laser and signal transmission, signal interference, and pressure and temperature dependence of the LIF signal. Different excitation strategies were compared within each vibrational band and across the different $A-X$ bands. It was shown that the choice of the excitation/detection strategy depends on the combustion condition, geometry of the combustion chamber, availability of laser equipment and an understanding of the global chemistry involved in the reaction. Among others, three excitation wavelengths (“DiRosa” transition at 226.03nm @ $A-X$ $(0,0)$ band, “B” transition at 235.87nm @ $A-X$ $(0,1)$ band and the “Schulz” transition at 247.94nm @ $A-X$ $(0,2)$ band) showed outstanding performance compared to others within each $A-X$ band. Discussions were based on spectrally resolved 1-D line imaging
measurements in premixed methane/air flames at 1–60bar with equivalence ratios of $\phi = 0.83–1.13$.

Second, absorption of UV light by CO$_2$ and subsequent emission of CO$_2$-LIF was identified as a major source for laser/fluorescence signal attenuation and detection interference, respectively. CO$_2$-LIF was investigated with excitation between 215 and 255nm with spectrally resolved 1-D line-imaging in 5–40bar premixed CH$_4$/O$_2$/Ar and CH$_4$/air flames. LIF of carbon dioxide consists of a broad (200–450nm) continuum with a faint superimposed structure. CO$_2$ absorption is the main source of attenuation for both the laser beam and fluorescent signal. In addition, CO$_2$-LIF can be a major source of interference during NO-LIF detection, since the broad emission features of CO$_2$ overlap with the $\gamma$ bands of NO. The interference from CO$_2$ is particularly enhanced for excitation wavelengths in the $A-X(0,1)$ band, and particularly for the $A-X(0,2)$ due to low levels of NO-LIF signal as a result of sparse population in the higher vibrational bands ($\nu'' = 1,2$) at combustion temperatures. As for using CO$_2$ LIF as a diagnostic tool, the signal from CO$_2$-LIF was found to be linear with pressure and laser fluence and potentially viable as an independent diagnostic tool for CO$_2$ detection; 2-D CO$_2$-LIF imaging using optimized excitation was demonstrated.

Third, an accurate temperature measurement technique for steady, high-pressure flames was proposed using excitation wavelength-scanned LIF with the NO $A^2\Sigma^+ - X^2\Pi (0,0)$ band. Excitation spectra were simulated with a computational spectral simulation program (LIFSim) and fit to the experimental data to determine gas temperatures. This “multiline NO-LIF thermometry” is robust against elastic scattering and broadband LIF interference from other species, and yields absolute, calibration-free temperature measurements. Temperature measurements were demonstrated in slightly lean ($\phi = 0.9$) CH$_4$/air flames for a range of pressures (1–60bar) and results were compared with an intrusive metal bead infrared thermometry. Good agreement for both temperatures was found for pressures up to 50bar. Multi-line thermometry can be an effective tool for studying high-pressure flame chemistry as well as providing a standard to evaluate and validate fast-imaging thermometry techniques for practical diagnostics of high-pressure combustion systems.
Finally, studies to optimize the detection strategies of 2-D NO-LIF imaging in high-pressure flames were investigated. A single laser and multi-camera detection strategy was proposed to isolate the NO-LIF of interferences from O_2 and CO_2. Design rules were presented to optimize the LIF detection wavelengths for quantitative NO-LIF measurements over a wide range of pressures (1−60bar) and temperatures. By scanning simulated detection filter functions over spectrally dispersed emission spectra, optimized detection bandpass windows were selected for excitation in the $A−X(0,0),(0,1)$ and $(0,2)$ bands of NO. Quantitative NO-PLIF images were demonstrated using 226.03nm in the $A−X(0,0)$ band using the multi-detection strategy. Concentrations of NO as a function of pressure were compared with numerical modeling (Chemkin Premix using GRI-Mech 3.0). The model was able to predict the change of NO as a function of pressure with slight discrepancies in the absolute quantity. In addition, it was shown that spectrally resolved 1-D line imaging offers the possibility of highly selective detection of NO-LIF down to extremely low concentrations (<10ppm) using only a one-laser and one-camera setup. The discussion and demonstrations reported in this dissertation provide a practical guideline for application of fast 1-D or 2-D NO-LIF imaging in practical high-pressure combustion systems with fluctuation and/or turbulent flow structures. Ultimately, the selection of excitation and detection strategies depends on the combustion characteristics, gas composition, system geometry, target sensitivity and availability of lasers and cameras. Results presented in Chapters 4 to 7 should empower the experimentalist to design a setup for detection of NO in practical high-pressure combustion systems and simultaneously allow for a preliminary assessment of expected sensitivity and SNR in the experiment.
List of References

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References


References


Appendix

1. Formation and Reburn of Nitrogen Oxides in Combustion

Formation mechanisms of NO have been extensively studied and are relatively well-known. NO formation (mostly from nitrogen supplied by the ambient air) and reburn reactions are counteracting, and their balance ultimately determines the final production of NO. Key reactions involved in these processes are summarized here. The discussions are based on articles by Bowman [6, 177] and textbooks of Glassman[187] and Warnatz [5].

1.1 Nitric Oxide Formation Mechanisms

There are three major sources of the NO formed in combustion: (1) the thermal NO mechanism, (2) the prompt NO mechanisms (HCN, N$_2$O and NNH mechanisms), and (3) the fuel-bound nitrogen mechanism.

**Thermal NO Mechanism (Zeldovich Mechanism)**

Three reactions comprise the thermal NO formation mechanism:

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

The rate-limiting step in the NO formation process is reaction (1), owing to its high endothermicity and associated activation energy (due to triple bonds of N$_2$). Using a steady-state approximation for N-atom and assuming that the O-atom concentration may be calculated from equilibrium considerations, the maximum NO formation rate can be expressed as,

\[
\frac{d[NO]}{dt} = 1.70 \times 10^{17} \cdot T^{1/2} \cdot \exp\left[-69750 / T(K)\right] \cdot [O_2]^{1/2}_{eq} \cdot [N_2]_{eq} mol / cm^3 s
\]
As can be seen from equation (4), thermal NO is strongly dependent on temperature; it is generally the dominant source of NO production in high-temperature flames. In addition, it may be seen that the thermal NO production in terms of mole fraction increases with pressure ($\sim \sqrt{p}$).

**Prompt NO Mechanism: HCN Mechanism**

NO can be produced when nitrogen reacts with CH radicals in the flame to produce HCN, NCN, H and N radicals as follows,

\[
\begin{align*}
\text{CH} + \text{N}_2 & \leftrightarrow \text{HCN} + \text{N} \quad (5) \\
\text{CH} + \text{N}_2 & \leftrightarrow \text{NCN} + \text{H} \quad (6)
\end{align*}
\]

Subsequent reactions of the product radicals (mostly with OH) lead to the formation of NO. The reaction rates of (5) and (6) are dependent on temperature and increase exponentially as temperature is raised. As pressure increases (>1bar), CH+N$_2$ reactions resulting in HCN$_2$ become dominant and the role of HCN$_2$ in the production of NO should be considered.

**Prompt NO Mechanism: N$_2$O Mechanism**

NO can be produced during reaction sequences when N$_2$O is formed and removed in the combustion gases by a third body recombination reaction (M=collision partner),

\[
\begin{align*}
\text{O} + \text{N}_2 + \text{M} & \leftrightarrow \text{N}_2\text{O} + \text{M} \quad (7) \\
\text{N}_2\text{O} + \text{O} & \leftrightarrow \text{NO} + \text{NO} \quad (8)
\end{align*}
\]

Nitric oxide formation by the N$_2$O mechanism increases as the fuel air ratio decreases or as the burned gas temperature decreases. In particular, NO formation increases with pressure due to the increase in the rate of third body collisions in (7). However, the N$_2$O lifetime at combustion temperatures (>1500K) is less than 10ms and hence reaction (8) is
not a significant production channel for NO for most practical premixed flames at low pressures.

**Prompt NO Mechanism: NNH Mechanism**

NO can be produced during the formation and removal of NNH radicals. The key reactions involved in this process are as follows.

\[
\begin{align*}
N_2 + H &\leftrightarrow NNH \\
NNH + O &\leftrightarrow NO + NH
\end{align*}
\]

While, the NNH mechanism can be a dominant source of NO production in low-pressure \( \text{H}_2/\text{Air} \) flames, its contribution is mostly negligible in high-pressure flames where the concentration of H radicals in the flame front is less.

**Fuel-Bound Nitrogen Mechanism**

A principal source of \( \text{NO}_x \) emission in combustion of fossil fuels comes from nitrogen that is chemically bound in the fuel itself. These fuel nitrogen species typically are aromatic compounds with one or more nitrogen atoms bound in the ring. The stable nitrogen-containing products formed as a result of the pyrolysis of the fuel are mainly HCN and \( \text{NH}_3 \). Hence, the mechanism for conversion of fuel nitrogen to nitrogen oxide will involve reactions of importance in oxidation of HCN and also \( \text{NH}_3 \). Fuel-bound nitrogen is of significance mostly in combustion of coals or other heavy fuels.

**1.2 Nitric Oxide Reburn**

NO can be removed by reacting with hydrocarbon radicals in the flame, and this process is called ‘NO reburn’. When sufficient fuel is supplied to the combustion process, the excess fuel remaining in the combustion products can lead to the creation of fuel-rich zones. As the fuel species reacts, a number of small hydrocarbon radicals (\( \text{CH}_3, \text{CH}_2, \text{CH} \) and \( \text{HCCO} \)) are produced that react with the NO to form cyano species, which in turn may react preferentially to form \( \text{N}_2 \). A slight increase of hydrocarbons in the flame can
lead to a drastic increase in the reduction of NO. NO reburn can occur via several channels and the specific elementary reaction steps that initiate the NO reburn process include,

\[
\begin{align*}
\text{CH}_3 + \text{NO} & \rightarrow \text{HCN} + \text{H}_2\text{O} \quad (11) \\
\text{CH}_3 + \text{NO} & \rightarrow \text{H}_2\text{CN} + \text{OH} \quad (12)
\end{align*}
\]

and

\[
\begin{align*}
\text{HCCO} + \text{NO} & \rightarrow \text{HCN} + \text{CO}_2 \quad (13) \\
\text{HCCO} + \text{NO} & \rightarrow \text{HCNO} + \text{CO} \quad (14)
\end{align*}
\]

At elevated temperatures, the reaction of NO with CH will contribute to NO removal via

\[
\text{CH} + \text{NO} \rightarrow \text{HCN} + \text{O} \quad (15)
\]

Subsequent reaction of the HCN produced in reactions (11), (13) and (15) preferentially leads to N\(_2\) formation under fuel-rich conditions. The H\(_2\)CN formed in reaction (12) can dissociate to produce HCN,

\[
\text{H}_2\text{CN} \rightarrow \text{HCN} + \text{H} \quad (16)
\]

and, therefore, contribute to the NO \(\rightarrow\) HCN \(\rightarrow\) N\(_2\) process. The HCNO formed in reaction (14) reacts primarily via

\[
\begin{align*}
\text{HCNO} + \text{O} & \rightarrow \text{HCO} + \text{NO} \quad (17) \\
\text{HCNO} + \text{OH} & \rightarrow \text{HCOH} + \text{NO} \quad (18) \\
\text{HCNO} + \text{H} & \rightarrow \text{HNCO} + \text{H} \quad (19)
\end{align*}
\]
Reactions (17) and (18) effectively regenerate the NO removed in (14) and do not contribute to the reduction of NO. However, HNCO produced from reaction (19) can react with O, H or OH to produce amine species (NH, NH₂), HNO or NCO that may undergo subsequent reactions to form NO or N₂O or to form N₂.

2. Operation Flow Rates for High-Pressure Burner

Stable operation of the high-pressure burner is dependent on the balance of combustion gases and coflow around the perimeter of the matrix for flame stabilization. The optimized flowrates used to stabilize a CH₄/air for various pressures (1–80bar) and equivalence ratios are listed in the following table. The three columns on the far right correspond to the NO seeding (NO flow) and N₂ balance levels (N₂ flow) for specific ppm of NO seeded (NO). Note that it does not correspond to the equivalence ratio in the second column and only varied as a function of seeding level for that specific pressure.

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<th>NO flow ppm</th>
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<td>200</td>
</tr>
</tbody>
</table>
For operation of the burner using alternative fuels (i.e., ethane, hydrogen etc.), the total flowrate and coflow for flame stabilization can be used from the above the table.